U. S. DEPARTMENT OF AGRICULTURE,

COLORIMETRIC, TURBIDITY, AND TITRATION METHODS USED IN SOIL INVESTIGATIONS.

BY

OSWALD SCHREINER AND GEORGE H. FAILYER.

WASHINGTON:

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Soils,
Washington, D. C., November 10, 1905.

Sir: I have the honor to transmit herewith the manuscript of a technical paper entitled " Colorimetric, Turbidity, and Titration Methods Used in Soil Investigations," and to recommend that it be published as Bulletin No. 31 of the Bureau of Soils.

Respectfully,

Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

PREFACE.

For several years past investigations which have required the exact determination of minute quantities of dissolved mineral substances have been in progress in the laboratories of this Bureau. The usual standard analytical procedures have not been applicable to this work. The dilution of the solutions (generally aqueous extracts of soils) has been high, and the total amounts of material available have not been sufficient, even when concentrated by evaporation, to yield quantities which could be determined with satisfactory precision. On this account it has been felt necessary to seek other methods which would prove sufficiently delicate and at the same time sufficiently accurate for the purposes in view. Considerable time and effort have been spent in collecting information about such methods, in adapting them, and in devising new ones. The results have been very gratifying. The use the Bureau has been making of these methods has attracted considerable attention to them not only from soil investigators, but also from water analysts and others whose work involves the estimation of minute quantities of dissolved mineral substances. In consequence of the increasing number of requests coming to the Bureau for detailed information concerning them, it has been deemed advisable to prepare a brief but comprehensive statement of these methods. The technical details which the experience of the Bureau's force has shown to be most advisable are presented in such a form that they can be readily followed by other analysts.

These methods require but a limited outfit in apparatus, so that temporary laboratories for field investigations can be readily established for their use, the necessary preparation of standards, etc., being controlled from a central laboratory. They are easily learned and followed by any one having manipulative skill and satisfactory eyesight, although but a limited acquaintance with chemistry. It should nevertheless be remembered that these methods are sensitive instruments and do require more than ordinary care in handling; that satisfactory results can not be expected until the analyst has trained himself in their use, and that on account of certain personal peculiarities which the analyst may possess it is not every one who can hope to use them satisfactorily. It can not be too strongly emphasized

that the analyst should test himself thoroughly before confidently applying these methods to any particular problem.

Not all of these methods are of equal delicacy, nor are they all of as great accuracy as could be desired. With some of them the Bureau has had but a limited experience. On the other hand, some of the methods are of great delicacy, capable of a high degree of precision; they have been repeatedly checked by numerous tests in the Bureau's laboratories, and are the best available methods for the purpose in view.

<div style="text-align: right">FRANK K. CAMERON.</div>

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COLORIMETRIC, TURBIDITY, AND TITRATION METHODS USED IN SOIL INVESTIGATIONS.

INTRODUCTION.

For several years the Bureau of Soils has been carrying on a series of studies in which the estimation of small quantities of mineral plant food constituents was of the utmost importance. Known colorimetric and other methods were adapted and new ones devised for this purpose. In this bulletin the methods which have been used in the investigations of the Bureau, together with some which are applicable to similar work, are described concisely for the convenience of those desirous of continuing these investigations or of carrying on new lines of inquiry.

The determination of small quantities of mineral substances is necessary in the chemical study of the soil moisture in its relation to crops. The soil moisture is the nutritive solution from which the plant obtains its mineral plant food constituents, and the study of the quantity of these constituents present at any time during the growing season of the crop or the rate of supply by the soil grains of these constituents to the soil moisture is obviously of the greatest agricultural importance. The ordinary gravimetric or volumetric methods can not be used in attacking some of the problems which are connected with a scientific study of the soil solution, unless exceptionally large quantities of material are used, involving an enormous expenditure of labor and time. Methods capable of determining such minute quantities as are involved in these investigations give, therefore, a ready means for attacking the difficult problems of the soil from a variety of different view points. Such methods are very serviceable in the study of the readily water-soluble salts in the soil in order to ascertain whether growing crops affect the concentration of the soluble plant food constituents of the soil; whether different yields of crops are in any way connected with these quantities of plant food constituents; whether good or poor systems of soil management influence the soluble salts in the soil to a degree corresponding to the observed differences in yield; whether the quantities and character of these soluble salts are measurably different in different soil types, and whether such differences can be correlated with their known crop-producing power. A further line of study to which these methods are applicable is the determination of the salts found in the sap of plants, with a view to ascertaining whether the concentration of the plant sap in the crop bears any relation in strength

and character to the water-soluble salts in the soil on which the crop is growing. The absorption of the mineral nutrients by plants from cultures of known strength can also be readily studied with these methods, and much valuable information can thus be obtained concerning the nutrition and the selective absorption effects of plants.

The study of the solubility of the minerals of the soil, as maintaining the soluble mineral plant food constituents in the soil moisture, is of the greatest significance. The solubility and hydrolysis of the ordinary rock-forming minerals, not only in water, but in solutions of various electrolytes, is therefore of great importance in throwing light upon the solubility of the minerals of the soil in pure water, in water charged more or less with carbonic acid, and in the solutions formed by the various fertilizer salts. The solubility of the rock-forming minerals, though continuous, is slow and, comparatively speaking, slight, and here again the determination of very small quantities of soluble salts is requisite. In addition to the solubility of the common rock-forming minerals, the slight solubility of the phosphates of the soil, such as iron, aluminum, or calcium phosphates, in pure water and in solutions of the various fertilizer salts, can also be studied by means of these methods. In this way it is possible to gain valuable information concerning the behavior of these substances in the soil and the effect of fertilizer salts upon them.

Underground, surface, drainage, or lysimeter waters have in the past been frequently studied in connection with soil and fertilizer problems. The methods described in this paper are very well suited for the determination of the small quantity of material usually found in such waters. It is also possible to study the movement of the water-soluble salts of the soil by capillarity, gravitation, or diffusion by means of these methods. Not only is it possible to study the amount of this movement, but also the differences in the rate of movement of the several fertilizer constituents and the effect of different systems of soil management upon the rate of movement.

Experiments on nitrification and denitrification in soils are readily carried on by means of the colorimetric methods for nitrates, nitrites, and ammonia.

The absorptive power of soils for mineral salts is important in the chemical study of the soil, and its investigation has been materially simplified by the use of these methods. It is possible to study not only the amount of absorption of different fertilizer salts, but also the rate of this absorption, and thus to gain a better knowledge of this interesting and important property of soils.

PREPARING THE SOIL SOLUTION.

If comparable results are to be obtained, it is essential in preparing the soil extract to follow as nearly as practicable a uniform pro-

cedure. The volume of water used and the time of its action are necessarily conventional. The ratio of five parts of water to one part of soil has been adopted in procuring solutions of the readily water-soluble salts in many of the soil studies. The mixture is agitated three minutes and allowed to stand twenty minutes before filtering. The exact procedure when the soil to be examined is still in the moist state as collected in the field varies slightly from that when it is air dried or oven dried. All results are, however, stated on a uniform basis, preferably on the dry soil. The results from a moist soil are not comparable with those obtained from a dried soil, although both be stated in terms of dry soil, owing to the fact that dried soils give a somewhat greater concentration of soluble salts in the soil extract.

From moist soil.—The moist samples taken from typical and comparable portions of the field are well broken up and mixed in a granite-ware basin or porcelain dish. Two 100-gram portions of this composite are then weighed out on a balance capable of weighing accurately to within 0.1 gram. One of these portions is for the moisture determination. It is thoroughly dried in an oven and the content of moisture thus obtained taken into consideration, if the results of the analyses of the solution are to be expressed in terms of the dry soil. The calculation to parts per million of dry soil is readily made by means of the following formula:

$$S = \frac{s\,(500 + W)}{100 - W}$$

where S is the parts per million of the dry soil, s the parts per million of the soil solution as found by analysis, and W is the amount of moisture, in grams, in the 100 grams of the moist soil sample used in making the solution as described below. If it should be desired to calculate the strength in parts per million of the actual soil moisture as found in the above moisture determination, the following formula is applied:

$$M = \frac{s\,(500 + W)}{W}$$

where M is the parts per million of soil moisture, s and W as in the previous formula. These formulas can be readily adapted to the scale reading of the colorimeter, with proper allowances for the standards and dilutions used. This will prove very convenient when many determinations are to be made.

Measure out 500 c. c. of water, and after transferring the other 100-gram portion of the moist soil to a mortar add enough of the water to make a thick paste, working well with the pestle so as to break down all granulations and to have the soil well puddled. The balance of the 500 c. c. of water is then added and the mixture well stirred with the pestle during three minutes. If more samples are to

be worked in the mortar, the mixture is transferred to a jar and is allowed to stand twenty minutes, during which the coarser particles settle. The supernatant turbid liquid is then poured into one of the filtering chambers fitted with a well-washed Pasteur-Chamberland filter tube, as described below.

From dry soil.—If the soil sample to be used is already air dry and it is desired to give the results in terms of the completely dried soil, it will be necessary to determine the amount of moisture still present by heating a 100-gram portion in the drying oven and making the proper allowance in the final calculation, using the formula given above. If the soil to be examined is oven dried, the whole composite is removed from the oven while hot and pulverized in a large mortar, screening through a 2-mm. sieve. A 100-gram sample is then weighed out and poured into a glass-stoppered bottle. Add 500 c. c. of distilled water to the soil in the bottle and shake vigorously for three minutes to insure a thorough puddling of the soil particles. The mixture is allowed to stand twenty minutes for the coarser particles to subside and is then filtered. The mortar may be used as described above, but it is more convenient to use the shaking bottle when working with dry pulverulent soils.

CONSTRUCTION AND OPERATION OF THE FILTERING APPARATUS.

For the filtration of soil solutions the filtering device designed by Briggs[a] for the use of the field men has been used, with certain modifications to make it applicable to the handling of a large number of samples in the laboratory. Pressure is employed to increase the rate of filtration instead of suction,

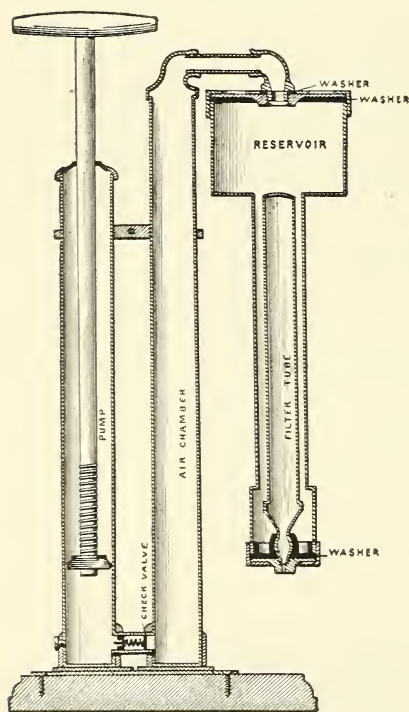Fig. 1.—Vertical section of small filter pump, showing piston, check valve, air chamber, filter reservoir, and filter tube.

as with the latter the maximum difference of pressure attainable is only one atmosphere. The construction of the single-barreled filter is shown in figure 1. The filter itself consists of an unglazed tube of

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[a] Bul. 19, p. 31, Bureau of Soils, U. S. Dept. Agr., 1902.

porcelain, such as is used in the Pasteur-Chamberland water filter. The tube is closed at one end, the other end being cemented in a glazed cap of porcelain, provided with a tubulure, which fits into a rubber gasket, as indicated in the figure. The filter tube is inclosed in a metal cylinder which serves as a receptacle for the solution to be filtered. The pump forces air through the check valve into an air chamber, so that a continuous pressure on the liquid can be maintained without constant pumping. The air chamber also serves as a support for the cylinder containing the filter tube. This form of the filter is very serviceable in the field work, where only an occasional solution is to be filtered, but where a large number of samples of soil are to be examined simultaneously in the laboratory it has been found necessary to construct a battery of filters. In Plate I, figure 1, is
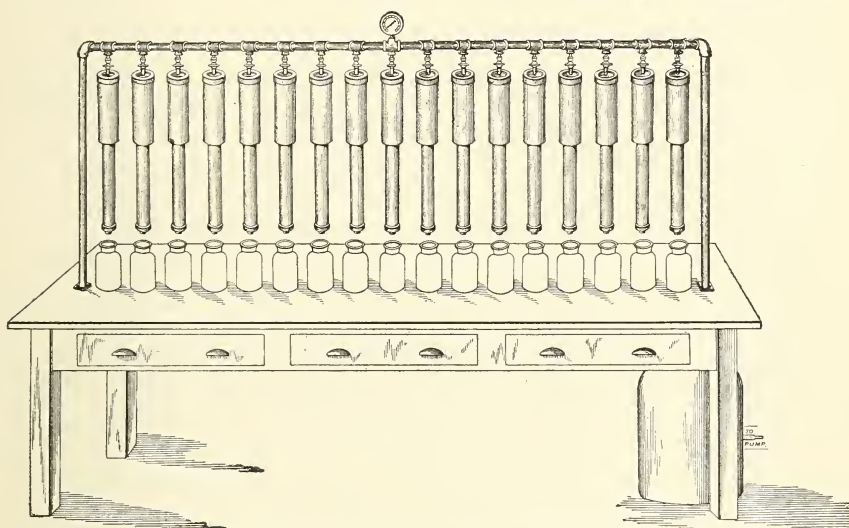
Fig. 2.—Front view of a large battery of filters for laboratory use.

shown a battery of four filters and also the single barrel pump shown in cross section in text figure 1. This battery was designed to meet the requirements of a small party of workers stationed at one place for a period of time. The air reservoir consists of a 7-gallon iron tank provided with four outlets, as shown in the figure. To these are attached short nipples threaded to fit the thread in the center of the cylinder head in the solution chamber. The opening on the side of the tank is fitted with a pet stop cock and a bicycle valve so as to hold the pressure in the tank. The pump is an ordinary bicycle pump having a cylinder of about $3\frac{1}{2}$ inches in diameter and a stroke of about $5\frac{1}{2}$ inches. The filter battery just described is very well suited to meet the demands of a small laboratory.

In figure 2 is shown a still larger apparatus designed entirely for

laboratory use, permitting the filtering of a large number of solutions at a time. The compression tank and pump are similar to those described above. The apparatus is provided with a pressure gauge. The cylinders which serve as reservoirs for the solution to be filtered have been made of several capacities to suit the work for which they were designed. In the small field pump the reservoir shown in figure 1 holds only 250 c. c. of solution, while the capacity of the longer cylinders shown in Plate I, figure 1, is 500 c. c. In the laboratory, where the preparation of large quantities of solution is frequently necessary, it has been found desirable to have the cylinders still longer, as shown in figure 2. The construction of the cylinders is shown in figure 3. They are nickel plated and burnished on the outside and either nickel or silver plated on the inside. This is especially important if the soil solutions are to be used for plant-culture experiments. The thread on the larger end of the cylinder must be true and have its plane at right angles to the axis of the cylinder, so as to secure uniform bearing on the rubber washer.

The turbid solution to be filtered is introduced into the cylinder by unscrewing the latter from the air chamber. After filling, the cylinder is again connected with the air chamber, and on pumping, a perfectly clear filtrate begins to flow out of the porcelain tubulure. The first 50 to 100 c. c. of the filtrate are discarded because the unglazed porcelain filter holds about 20 c. c. of water in the pore space. This also eliminates any error due to a slight change in the concentration of the solution owing to the absorptive effect of the filter itself on the first few cubic centimeters of solution. The remainder of the filtrate is then collected in a suitable vessel. The time of filtering the soil solution prepared as above described varies from five to twenty minutes, depending upon the amount of fine particles suspended in the liquid, which are deposited on the walls of the filter tube. With sandy soils the filtration is very rapid, even when only a moderate pressure is applied, but with heavy clays the fine particles so clog the filter tube that twenty minutes or more may be required to filter the solution, even with a pressure of 30 to 40 pounds per square inch.

FIG. 3.—Showing the construction of the filter chamber: A, metallic cylinder; B, rubber washer; C, cylinder head; D, screw collar; E, rubber nipple for holding filter tube; F, nipple plate; G, screw collar.

* The filter tube can be easily removed for cleaning by unscrewing the cap at the bottom and withdrawing the rubber gasket and tube.
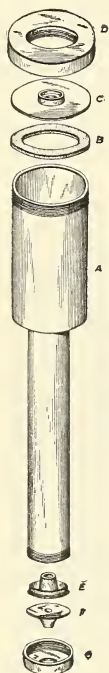
The fine deposit of clay is removed by washing in water, using a small brush with stiff bristles, and taking care to have the tubulure well protected so as not to get any of the water into the tube. It is then rinsed in distilled water. After cleaning the metal cylinder the tube is again fitted into it and distilled water passed through it by connecting with the pressure apparatus. Thus cleaned it is ready for use with the next solution.

When the filter tube has been used for some little time, its efficiency will be greatly impaired and the filtration becomes very slow. This is especially marked in dealing with soils rich in organic matter and with plant solutions, and is due to the development of bacterial life within the pores of the filter tube. The difficulty is, however, very easily overcome by drying the tube and then heating to redness for about half an hour. This is most effectively done by hanging the tube with the tubulure upward in a cylinder 9 cm. in diameter and 33 cm. in length made of galvanized iron and covered with asbestos, and partially closed at the top and bottom with asbestos rings. A single Bunsen burner introduced at the bottom will heat the filter tube to redness in a very short time. It is not necessary to burn out all organic matter, as even mere charring will open up the pores of the filter tube. After cooling, the filter tube is connected with the apparatus and well washed with distilled water. The first portion will usually be found to be highly colored because of the charred organic matter. This treatment of the tubes restores them to their former efficiency. In the study of plant solutions it becomes absolutely necessary to burn out the filters quite frequently, and in the study of the nitrates of the soil it is also highly essential that the filter cores be kept free from denitrifying organisms by this means.

DECOLORIZING THE SOIL SOLUTION.

Nearly all colorimetric work demands a colorless solution. If the solution is to be treated in any way in order to get rid of all organic matter, as, for instance, by the ignition in the potassium method, it need not be colorless, but in many of the other methods this is an absolute necessity. A colorless solution is not always obtained directly from the soil, especially if it has been recently or heavily manured. Moreover, samples which have been dried out in the laboratory frequently give colored solutions, though samples of the same soil fresh from the field give colorless solutions. The color may, however, be readily removed in most cases either by adding carbon black to the soil itself, so as to have it present during the shaking process, or, better, though with more loss of time, by adding it to the solution after filtration. It is usually sufficient to add 3 to 5 grams of the carbon black to 500 c. c. of the solution, shaking at intervals during twenty minutes and then filtering. This usually gives a perfectly colorless

solution, but it should always be tested by comparison with distilled water in colorimeter tubes.   If not completely colorless it can be subjected to a second treatment with carbon black.

There seems to be a widespread impression that only animal charcoal is capable of decolorizing solutions.   Animal charcoal, even when specially treated, still contains so much mineral substance that its use in the study of such dilute solutions of mineral plant nutrients as are here under investigation is quite prohibitive.   In the search, therefore, for a means of decolorizing the solutions with materials free from mineral matter it was found that some of the carbon blacks of commerce were quite effective in this respect.   These carbon blacks are prepared on a large scale by the partial combustion of petroleum or natural gas and deposition of the finely divided carbon on cooled surfaces.   Not all carbon blacks possess this property of decolorizing solutions, nor are they equally effective, and it is therefore necessary to test each brand specially for this property.   The brand used in the work of the Bureau has been the " G. Elf " carbon black.[a]   It has been found that the use of this carbon black does not measurably affect the extract, either by the addition of impurities or by the absorption of mineral substances from the solution.   Owing to its method of preparation the carbon black contains some oily bodies of the paraffin series.   This oily matter can be removed, if desired, by treating the carbon black with hot distilled water and removing the oily scum. The carbon black is then allowed to settle and the water is poured off as far as possible.   By repeating this treatment several times, finally collecting on a filter and drying, a carbon black almost entirely free from the oily matter can be obtained.   It has been found very desirable not to dry the carbon black completely, as it is more readily handled when slightly moist than when in the form of a dry, light powder.

OTHER METHODS FOR OBTAINING SOIL SOLUTIONS.

It has been found possible to obtain some of the actual soil water from the moist soil by means of a high centrifugal force.   Dr. L. J. Briggs and Mr. J. W. McLane of this Bureau have constructed for this purpose a centrifugal machine which consists of three concentric cylinders, the middle one having fine perforations.   The moist soil sample, as collected in the field, is put between the perforated middle cylinder and the inner cylinder.   The system of three cylinders is then rotated at a speed approaching 8,000 revolutions per minute. The soil moisture is thrown through the perforations and collects in the compartment formed by the perforated middle cylinder and the outer cylinder.   The solution is usually perfectly clear and needs no
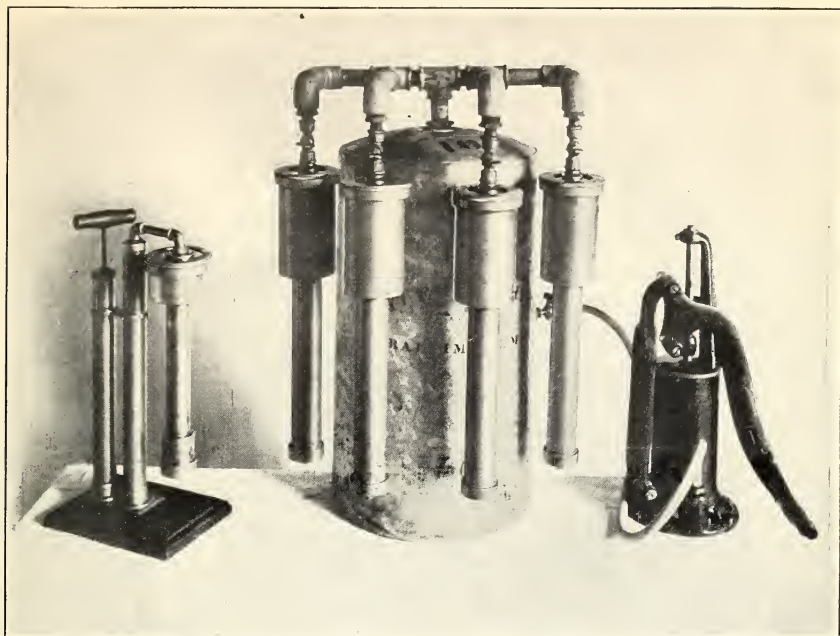

FIG. 1.—SINGLE CYLINDER FILTER WITH PUMP ATTACHED, AND A BATTERY OF FOUR FILTERS ATTACHED TO A COMPRESSED-AIR RESERVOIR PROVIDED WITH A PUMP.

FIG. 2.—SHOWING WIRE-NET FRAME FOR PARAFFIN BOTTLE, AND BOTTLES COATED AND READY FOR USE.

subsequent filtration. By this means it has been possible to reduce the soil moisture to approximately the optimum condition for plant growth, and this method of obtaining the actual soil moisture is therefore limited to soils containing more than the optimum. Nevertheless it has been possible to gain some valuable information concerning the actual concentration of the free soil moisture by means of this method, although for any extensive study the amount of solution that can be obtained is comparatively so small as to be practically prohibitive.

Another method for obtaining the free soil moisture direct is by means of the apparatus used by Briggs and McCall [a] in studying the capillary movement of soil moisture. The apparatus consists of a Pasteur-Chamberland filter tube connected by means of lead tubing to an exhausted 2-liter bottle. Air-tight connections are readily made by the use of short lengths of red rubber tubing, well coated with thick cotton-seed oil. Preparatory to placing the filter tube in the soil, a core of soil is removed by means of a tube, the external diameter of which is equal to that of the smaller end of the porcelain tube. The filter tube is slightly conical in form, so that when it is forced into this hole a good capillary connection is established between the walls of the tube and the soil. The apparatus is usually allowed to stand for about twenty-four hours, when the exhausted bottle is detached and the soil water which had been drawn into the apparatus is removed. The porcelain tube is not disturbed in removing the water, but the latter is drawn into a small flask by suction through a fine tube extending to the bottom of the porcelain tube.

Here, as in the preceding method, the apparatus is able to remove water from the soil only when it is comparatively wet, and is therefore not applicable to the study of the soil moisture during conditions approximating a drought.

PREPARING AND DECOLORIZING THE PLANT SOLUTION.

The plant solution may be prepared from either the green or the dry plant. Both give highly colored solutions, but with the use of carbon black perfectly colorless solutions are usually obtained.

From green plant.—The green plant sample is cut into fine pieces and thoroughly mixed. A 100-gram and a 20-gram portion of this composite sample are weighed off. The 100-gram portion is used for making a moisture determination, and the result is taken into account if the analysis of the solution is to be expressed in terms of dry matter or of plant moisture. The 20-gram portion is transferred to a porce-

[a] Science, N. S., **20**, 566 (1904).

lain or Wedgewood mortar and reduced to a fine pulp with the pestle. A little of a 500 c. c. portion of distilled water is added to the pulp and worked for one minute; the balance of the water is added and the mixture stirred with the pestle for three minutes. The solution is then strained into a jar or bottle for decolorizing.

The solution prepared from the fresh plant is always colored green by the chlorophyll. This is readily removed by carbon black. The solution obtained as above described is treated with 5 grams of carbon black (see p. 16)·and the mixture is shaken at intervals during twenty minutes, and then filtered through a Pasteur-Chamberland filter, discarding the first 50 c. c., as already described for the soil solution.

From dry plant.—The dry plant sample is taken from the drying oven and while still crisp is ground in a mortar or mill to a fine powder. A 10-gram portion of the well-mixed sample is put into a glass-stoppered bottle, and after adding 5 grams of carbon black and 500 c. c. of distilled water the mixture is well shaken for three minutes. It is then allowed to stand twenty minutes, with an occasional shaking, and filtered through a Pasteur-Chamberland filter, discarding the first 50 c. c.

The dry plant when not treated with carbon black yields a solution which is darker in color than that from the green plant. When the plant sample has been carefully dried, so as to still retain its green color, no difficulty is experienced in getting a colorless solution by using the carbon black. If the plant sample has been overheated, however, the resulting solution is very dark, and in some cases it is very difficult to remove all of the coloring matter from solution by means of carbon black, even if larger amounts and several treatments are resorted to, thus showing the necessity of drying the samples very carefully.

As pointed out in the description of the filtering apparatus, immediately after using the filter tubes they must be thoroughly cleaned and washed. They are subject to clogging through the development of organic life in the pores of the filters, but their efficiency is readily restored by burning and washing the tubes as described on page 15. As the plant solutions are appreciably greater in concentration than the soil solutions, it is advisable to keep a separate lot of filters for the plant work. If a filter tube used in the plant work is to be used for filtering soil solutions it should always be burned and well washed with distilled water until the filtrate has an electrical resistance comparable with that of the distilled water.

COLORIMETRIC METHODS.

In devising colorimetric methods there have been two main objects throughout, namely, speed and the ability to estimate small quantities, both of which are common to many of the methods, but not

necessarily so. A colorimetric method may have speed and yet not be capable of estimating very small amounts. Speed is, through necessity, perhaps, of greatest importance to the works chemist and to the busy analyst. The ability to estimate very small amounts of material, however, is of the greatest importance to the modern investigator in the field of the pure and applied sciences, and to him speed is of only secondary importance, if, indeed, he values it at all. Some of the more recently devised colorimetric methods are fully as laborious and perhaps even more tedious than the gravimetric methods, and their one virtue lies in the fact that they can be used in determining amounts so small that gravimetric methods fail, and hence they present a means of attacking problems which hitherto have been impossible of investigation.

The question whether a gravimetric or a colorimetric method should be used in a given case arises, therefore, almost entirely in connection with the class of colorimetric methods which have been devised for speed. The question in such a case is usually one of comparative accuracy as balanced by a gain in time. This gain in time may, however, be of the utmost importance not only in a works laboratory, but also in a scientific investigation where it is necessary to know the amount of substance present at any given time in the course of an experiment. In the second class of colorimetric methods no choice between a gravimetric and a colorimetric method exists when small amounts are involved. When larger quantities are available the choice should always be in favor of the gravimetric method, providing, of course, a reliable gravimetric method exists for the particular substance under investigation. When speed is also a characteristic of the method this will somewhat complicate the choice between a gravimetric and a colorimetric method, and the needs of the immediate problem under consideration must guide the analyst in his choice.

As to the accuracy of the colorimetric methods no general statement can be made. Some colorimetric estimations have been brought to such a degree of perfection that they far surpass gravimetric determinations in accuracy. On the other hand, many of the colorimetric estimations are only gross approximations; but even these serve a purpose, for in such cases we usually have no other means of estimating the substances. It is, however, between these two extremes that the majority of the methods lie. Folkard,[a] Krüss,[b] and many others have pointed out the extreme degree of accuracy which is attainable with such methods when carried out with care, and there is little doubt that their accuracy is more frequently underestimated

[a] Chem. News, 75, 73 (1897).
[b] Kolorimetrie u. Quantitative Spektralanalyse (1891).

than overestimated. This is due to a number of causes, chief among which are the inability on the part of many persons to judge colors accurately, contamination while making the tests, the use of impure reagents, and the employment of faulty apparatus. Practice will do a great deal to enable one to make good comparisons, but it can never make up for even a dulled color impression in the eyes of the operator. Great attention should be given to this point, and the operator should test himself thoroughly by matching a standard against itself in several degrees of intensity. If no concordant results can be reached by practice in this way, it is useless to go farther with this color, but it may, nevertheless, be possible for him to read accurately some other color. The use of impure reagents and contamination while carrying out the test are, of course, inexcusable. In carrying out accurate tests it is highly essential that the standard solutions be carefully prepared and protected from any contamination. This is especially true in the case of the ammonia and nitrite standards, the phosphate standard, where contamination by silica is very apt to take place, and many others. In some cases deterioration of the standard itself must be carefully guarded against. The solutions must be perfectly clear, with no suspended particles whatever. They should both be at the same temperature, since the intensity and the absorption spectrum of colored compounds and consequently the color of the solution change with the temperature. The solvent itself has an absorption effect on the light, and hence it is always advisable not to have the concentration of the unknown solution vary widely from that of the standard. It is better in this case to dilute the standard to a similar order of intensity with freshly distilled water. By this procedure the colors are likewise better compared, as the absorption spectrum and consequently the transmitted color of many of the dyes is quite different in concentrated solutions from what it is in more diluted solutions.

Mention is made in several places in this bulletin of the storing of reagents in paraffin bottles to prevent contamination by the solubility of glass. This contamination may be avoided by heavily paraffining glass bottles, but the paraffined wire pots, used in plant-culture work, as described in Bulletin 23, suggested the use of wire net as a framework for constructing a paraffin bottle, shown in Plate I, figure 2. For this purpose a galvanized iron net of one-eighth inch mesh is cut and formed into the desired shape, wiring or soldering the edges together, thus forming a very strong framework. This is then dipped into melted paraffin, finally flooding the inside with melted paraffin until a sufficiently strong-walled bottle has been obtained. These bottles are very serviceable for the storing of reagents in the magnesium, phosphate, and silica methods, and also as containers in determining the solubility of rock-forming minerals. Such bottles

would seem to be very well suited for shipping and storing hydro-fluoric acid and also alkaline solutions generally. Heavily nickel-plated teakettles have been found to be very convenient as metallic containers for the redistilled water used in the above-mentioned colorimetric methods. The water can be readily heated when it is required hot, and is drawn through a block-tin syphon tube which is inserted through the spout of the kettle.

The apparatus used in colorimetry is of importance in carrying out accurate tests and merits some consideration, not only from this point of view, but also from that of speed. A large number of colorimeters have been devised, but it would be impracticable to discuss the various forms here, and it must therefore suffice to outline briefly the three types of apparatus and procedures in most common use. In one of these the comparison vessels consist of a pair of parallel walled tanks into which the standard solution and the unknown solution are put and then diluted until they are of equal intensity. In this type, then, the length of column viewed by the observer remains constant and the equality of color is regulated wholly by dilution. The comparison is made in a suitably constructed camera. This general procedure is accurate but rather tedious.

A second type of procedure, and the one usually followed in water analysis, has many objections and is likewise tedious, if very accurate results are desired, as it involves a great many separate tests and comparisons. It consists in developing the color in equal volumes of the unknown solution and of solutions of known strength, selecting the ones which come nearest to it in intensity and then repeating, this time within narrower limits, until a strength of known solution is found which exactly corresponds with that of the unknown. The apparatus used for making the comparisons consists of glass cylinders, preferably with polished glass bottoms, on which have been etched capacity marks, such as " 25," " 50," or " 100 c. c." Such tubes as are found on the market are very faulty in their construction and only too often are made of very poor and tinted glass. The bottoms are exceedingly irregular and the capacity marks vary greatly in their height from the bottom of the tubes, so that it is highly essential that only well " matched " pairs of cylinders be used in making tests. Moreover, the tubes are usually somewhat tapering, so that the lower 50 c. c. will occupy an entirely different height from the upper 50 c. c. This difference in height amounts to as much as 10 per cent in tubes obtained from the most reliable firms. It is, of course, the length of the column of liquid and not the volume which determines the intensity of the image viewed, and in such cases the operator is, therefore, always dependent upon the coincidence of both volume and height in the tubes used—in other words, he must have a pair of well-matched tubes.

In the third procedure the height of the standard column is changed until the intensity is the same as that in the unknown solution when looking through the columns. This is by far the most speedy and, when the proper conditions are observed, also the most accurate of the procedures mentioned. This change in the heights of the solution has been accomplished in a variety of ways; by dropping from a burette into one of the above tubes, by providing such a tube with a stopcock at the bottom, by connecting by means of a side tube at the bottom with a reservoir which allows moving the liquid up or down at will, and by means of an immersion prism or tube. Curiously enough the graduation into cubic centimeters has been carried over to the cylinders used in many of these instruments when it is perfectly obvious that it is the height of the standard liquid which determines the strength of the unknown solution. The use of the cubic centimeter scale in graduating such colorimetric apparatus is entirely wrong in principle and should be abandoned. A rational graduation into scale divisions independent of capacity, and therefore of the size or uniformity of the bore of the tube, is used in one of the instruments described below.

DESCRIPTION AND USE OF COLORIMETERS.

An instrument similar to that described and illustrated by Whitson [a] was used in the earlier work of the Bureau. It consists of (1) a measuring tube of colorless glass about 26 mm. in diameter and 26 cm. in length, with a side-delivery tube near the bottom to connect by means of a rubber tube with a sliding reservoir for quickly changing the length of the column of the standard colorimetric solution; and (2) a comparison tube, also of colorless glass and as nearly as practicable of the same dimensions as the measuring tube. Both tubes have accurately ground and polished bottoms. The whole is mounted in a suitably constructed camera, shown in figure 4. The reflector at the top of the instrument is adjusted so as to reflect the light from the sky, preferably a north light, through the columns of the liquid in the tubes standing on a shelf provided with circular openings, then passing to the mirror at the bottom, where it is reflected to the eye of the observer. The reservoir containing the standard colorimetric solution is then moved up or down until the two circular images seen in the lower mirror are of equal intensity.

In this form of apparatus the previously mentioned irregularity in the bore of the tubes becomes a vital defect when a cubic centimeter scale is used. The following conditions must, therefore, be complied with in graduating such a pair of tubes, if they are to be used for accurate work. The comparison cylinder A must be of a uni-

form bore, a condition not easily met. On this are etched a 50 and
a 100 c. c. mark. The height of the 100 c. c. mark is laid off on the
measuring cylinder *B*, which is to contain the standard colorimetric
solution and is provided with the outlet at the bottom. The distance
from this mark to the bottom of the tube is divided into 100 equal
divisions. In other words, the scale on the standard solution tube *B*
is really the scale which reads cubic centimeters in the unknown
solution tube *A*. If, therefore, the latter should be broken, the
graduated tube has lost its value, for it would be difficult to find
another tube which would correspond to this scale. Two distinct
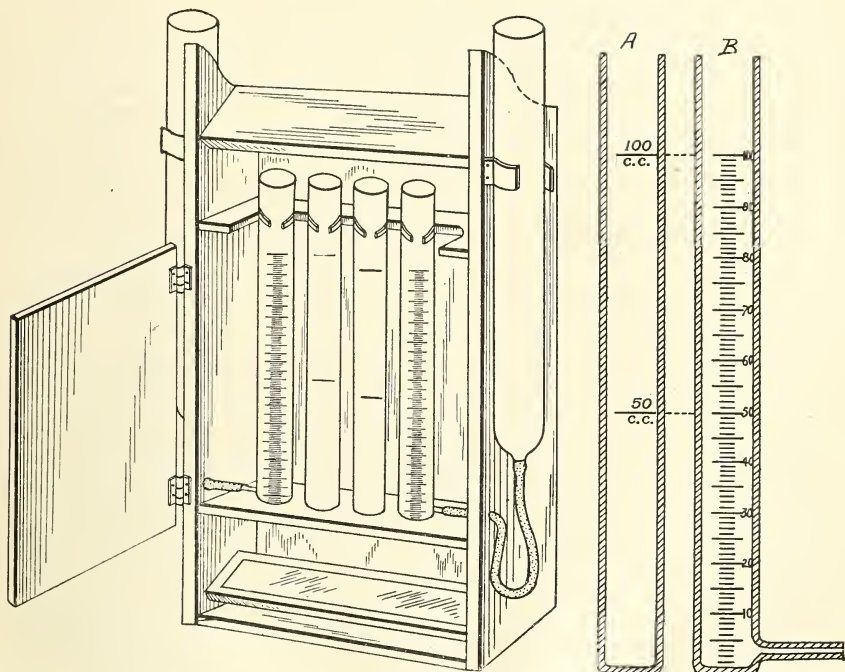
Fig. 4.—Colorimeter with two sets of apparatus and a pair of tubes showing graduation:
A, comparison tube; *B*, measuring tube.

pairs of such tubes are in the camera shown in figure 4, and it is
obvious that the tubes can not be interchanged.

In using the colorimeter, the solution to be compared is poured into
the comparison tube and need not be made up to definite volume.
The standard colorimetric solution is poured into the reservoir. The
intensity of the two images seen in the lower mirror is then com-
pared and the reservoir moved until the images appear of equal in-
tensity. The height of the standard is then read off by opening the
door, which was closed while making the setting. The length of the
column is then changed in the opposite direction and another setting
made. The reading should consist of an average of at least three

settings. The reading thus obtained, when multiplied by the amount of active substance in each cubic centimeter of the standard colorimetric solution, gives the amount of active mass in solution in the comparison tube.

Besides the previously mentioned difficulties in connection with colorimeter tubes provided with cubic centimeter scales, this apparatus has some minor defects, chief among which is the inability to have the liquid in the tube respond instantaneously to the motion of the reservoir. Some little time is always required for the liquid to flow through the rubber tube, and it is therefore impossible to make a setting by oscillation above and below the exact point. Such oscillation is desirable, as the eye is more sensitive to changes in color than to equality of color. In this instrument the equality of color is therefore approached from above and below alternately in making different settings. Another objectionable feature is the rubber tube itself, which is affected somewhat by the colorimetric solutions, such as the nitric acid solution in the phosphate work and the alkaline solutions of the nitrate work or in the determination of ammonium. This action on the rubber is especially objectionable in a laboratory where all these determinations are to be made, and necessitates either the use of a separate set of apparatus or the changing of the rubber tubes for each different series of tests.

These objectionable features are in a large measure overcome in the colorimeter recently described by Schreiner,[a] and this is the form now used in this laboratory. The working parts of the instrument— that is, those parts which come in contact with the solutions—are entirely of glass, mounted in a suitable camera of wood, as shown in figure 5. Another form of the colorimeter is being constructed in which the tube supports are made of metal instead of wood. In this apparatus the entire system of tubes can be revolved about a vertical axis, permitting of changing the relative position of the images at will, thus avoiding the possibility of an error resulting from inequality in illumination.

In its simplest form the colorimeter consists essentially of graduated glass tubes containing the standard and the unknown colorimetric solution, the column of liquid in both tubes being changed by means of two smaller immersion tubes, also of glass. The immersion tubes, A, are 26 cm. in length and about 2 cm. in diameter and resemble the narrow Nessler tubes, the bottoms being well ground and polished. The upper ends of the tubes are mounted in blocks of wood, which fit into grooves on the body of the colorimeter. This permits the ready removal of the tubes from the colorimeter for cleaning when the liquids are changed. The graduated tubes, B,

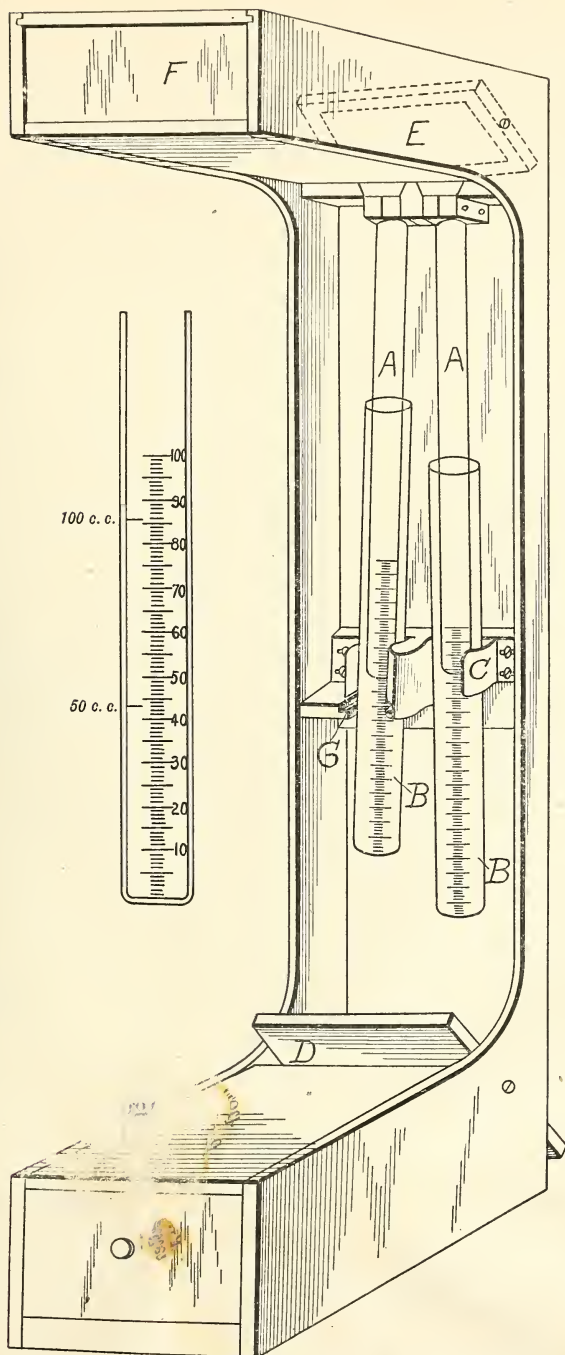a Jour. Amer. Chem. Soc., 27, 1192 (1905).

FIG. 5.—Colorimeter with a tube showing graduation: *A*, immersion tubes; *B*, gr͏
tubes; *C*, brass clamp; *D*, reflector; *E*, mirror; *F*, opening for viewing th͏
G, slot for insertion of standard glass slides.

have well-ground and polished bottoms and are likewise 26 cm. in length. but have a diameter of about 3 cm. The scale divisions are 2 mm. apart. On the reverse side of the tube there is a 50 c. c. and a 100 c. c. mark for making the solutions up to a definite volume. These tubes are supported by a block of wood about midway of the camera and are held in place by brass springs or clamps. C, the tension of which can be regulated to suit the diameter of the tube, so as to allow it to be moved freely up or down by hand and yet be firmly held in position when the setting is made. It will be noticed from the figure that the glass tubes diverge slightly at the bottom. This has been found of advantage. as it allows the operator to look down the center of both immersion tubes as well as to bring the upper parts of the tubes closer together. The openings to the immersion tubes can be covered by means of a microscope slide to prevent dust from falling into the tubes. The tubes are illuminated from the reflector, D, below. which carries a white sheet of cardboard or opaque glass, and after passing through the tubes the light is reflected by a mirror, E. in the upper part of the instrument to the eye of the observer at F. The mirror. E, should. as far as practicable, be of colorless glass. as the greenish color of ordinary glass has a tendency to change the quality of the light and to interfere in the estimation of weak solutions. This is especially true of the yellowish-green color of the phosphomolybdate solutions obtained in the estimation of phosphate. The dimensions of the camera are about 70 x 32 x 16 cm.

To make the comparison. the standard colorimetric solution is poured into one of the graduated tubes and put into place in the camera, together with the immersion tube. The unknown colorimetric solution, made up to definite volume, is put into the other graduated tube and similarly placed in the instrument. The tube containing the solution of unknown strength is set at a convenient height. say 40 scale divisions, and the other tube containing the standard moved up or down, the operator watching the effect on the images in the mirror through the opening at the front of the camera. By moving the standard tube so that the image is alternately weaker or stronger than that of the unknown solution the setting can be accurately and quickly made. When both images show the same intensity of color the setting is read by noting the division mark on the graduated tube opposite the ground bottom of the immersion tube. This reading will give the height of column of the standard, which exactly corresponds with the intensity of color of the column of the unknown solution. It follows that the strengths of these two colorimetric solutions are inversely as the heights of the columns—that is, the readings on the two tubes. If R is the reading of the standard

solution of strength S and r the reading of the colorimetric solution of unknown strength s, then

$$s = \frac{R}{r} S.$$

The same formula, of course, applies when the standard is fixed and the unknown solution moved up or down until the images are of equal intensity.

Below are given three concrete examples. In the first the solution is of the same order of concentration as the standard; in the second the solution is much stronger than the standard; and in the third the solution is considerably weaker than the standard:

Example 1.—A 50 c. c. portion of a solution was evaporated and treated according to the directions given for the determination of nitrates, the colored solution being made up to 50 c. c. On comparing this in the colorimeter with the 1 part per million standard it was found that a reading of 40 divisions corresponded to a reading of 50 of the standard. The strength of the colored solution is therefore, $s = \frac{50}{40} \times 1 = 1.25$ p. p. m. NO_3. The strength of the original solution is in this case the same as the strength of the colored solution.

Example 2.—A 25 c. c. portion of a solution was evaporated and treated according to the directions given for the determination of potassium. On developing the color it was found to be very intense, and when completely developed the solution was made up to 100 c. c. The solution was still too deeply colored for accurate measurement, and 25 c. c. were taken and diluted to 100 c. c. On comparing this in the colorimeter with the 1 part per million standard it was found that a reading of 40 divisions corresponded to a reading of 36 of the standard. Therefore $s = \frac{36}{40} \times 1 = 0.9$ p. p. m. K in the colored solution read. From the above dilutions it is obvious that the original solution is 16 times as strong as the colored solution used in making the reading, i. e., $0.9 \times 16 = 14.4$ p. p. m. K.

Example 3.—A 100 c. c. portion of a solution was evaporated and treated according to the directions given for the determination of phosphate. The color of the 50 c. c. of colorimetric solution obtained was found to be too faint for accurate measurement against the full standard of 10 parts per million. The standard was therefore diluted to half strength with silica-free water and the comparison then made in the colorimeter. It was found that a reading of 24 of the 5 parts per million standard solution corresponded to a reading of 40 of the unknown solution. Therefore $s = \frac{24}{40} \times 5 = 3.0$. Since only 50 c. c. of colorimetric solution were obtained from 100 c. c. of the original solution, it follows that the strength of the latter is only one-half of the colored solution, i. e., 1.5 p. p. m. PO_4.

Standard glass slides may be inserted at G below one of the immersion tubes in place of the tube containing the standard solution, the immersion tubes being retained so as to give similar images when viewed from above. Lovibond [a] slides have been used for this purpose, the constant C for the slide being obtained by the following formula:

$$C = R S,$$

[a] Lovibond, Jour. Soc. Chem. Ind., **13**, 308 (1894) ; see also Schreiner, Pharm. Review, **19**, 61 (1901).

where R is the reading of the standard of strength S when the two images are of equal intensity. The simple color slides can be used in some cases, such as the yellow for the nitrate method, but usually a combination of color slides will be required to match the color of the solutions, and this complicates the use of the slides considerably. A series of slides of different intensities, but bearing a simple relation to each other, is necessary in order to measure both strong and weak solutions. The strength s of the unknown colorimetric solution, when measured against a slide, is found by the formula

$$s = \frac{C}{r},$$

where C is the above-mentioned constant for the slide used and r the reading of the unknown solution. These slides are especially serviceable as a control for checking the standard solutions from day to day where the use of the latter is preferred.

The glass parts of the colorimeter have been made for the Bureau according to the following specifications: The measuring colorimeter tubes are to be 26 cm. long, with *inside* diameter as nearly as practicable 27 mm.; in no case less than 25 mm., and not greater than 29 mm. The glass is to be colorless, and the bottoms well ground and polished, with the internal surfaces of the bottoms plane, in no case appreciably convex or concave. The bottoms to be ground down sufficiently to make the ground surface a little larger than the internal diameters of the tubes; each of the tubes to be provided with an etched scale of 100 2-millimeter divisions. The scale to begin at the level of the inner surface at the bottom, the length of the marks being 6 mm., and every fifth mark 12 mm., numbering every tenth mark, on the right side, 10, 20, 30, etc., beginning at the bottom. On the reverse side of each measuring tube there are to be etched two capacity marks, one for 50 c. c., and the other for 100 c. c. The smaller tubes are likewise 26 cm. long, with *outside* diameter not greater than 20 mm., and not less than 18 mm., with the thickness of the glass the same in all the tubes. The bottoms of these tubes are to be carefully ground and polished, and the inside of the bottom never sensibly convex or concave. They must be of colorless glass with the bottoms so ground that the diameter of the ground portion exceeds the internal diameter of the tube. These tubes are to be provided with neither scale nor capacity marks.

The tubes furnished by the makers of glass apparatus leave much to be desired. According to the statements of these makers, the bottoms of the tubes can be ground and polished on the outside only, and this leaves the inner surface uneven and slightly concave. For very accurate work, tubes with bottoms formed of plates of plane glass cemented on are strongly recommended, as the images obtained in

this case are perfectly bright and free from all the objectionable features introduced by light passing through the uneven and somewhat concave bottoms of the ordinary tubes, which act as plano-concave lenses. The objectionable feature is the cement, which with continued use of the alkaline or acid media of many of the colorimetric solutions is rapidly disintegrated, and the tube will have to be replaced by another until repaired. When a colorimeter is in almost continued use this loosening of the cement is very troublesome, and the more faulty tubes with permanent glass bottoms, above described, have been found on the whole to be the most satisfactory for routine work. Mr. A. B. Depuy, of this Bureau, is working on a method for grinding and polishing the inner surface of these tubes and is meeting with fair success, having produced some good tubes.

DESCRIPTION OF THE COLORIMETRIC METHODS.

Ammonium.

The ammonium is determined by means of the well-known Nessler reaction, as used in water analysis. The method consists in adding to the clear and colorless solution to be tested an alkaline solution of mercuric potassium iodide, known as Nessler reagent. The alkali of the reagent liberates the ammonia from its salts, and when a considerable quantity of the latter is present a precipitate is formed, but in dilute solutions the compound remains in solution, giving a yellow color. The intensity of color is proportional to the amount of ammonium present and is compared with that of a dilute standard ammonium chloride solution similarly treated. The substituted ammonias give a similar precipitate and color with this reagent, and it might be necessary to take this fact into consideration in some lines of work.

Reagents required.

1. *Ammonia-free water.*—This may be prepared by redistilling the water of the laboratory after acidifying slightly with sulphuric acid, or by simply redistilling without the addition of acid until a 100 cubic centimeter portion no longer gives a reaction with Nessler reagent (3), and then collecting the distillate until about one-fifth of the original volume remains in the still. For colorimetric purposes it can be very quickly prepared by adding sodium carbonate to the distilled water of the laboratory until slightly alkaline and boiling until about one-fourth has evaporated. The residual water is cooled and is then ready for use. Ammonia-free water is used in the preparation of the following reagents and wherever contamination by ammonia will influence the result.

2. *Sodium carbonate solution.*—A boiled saturated solution.

3. *Nessler reagent.*—Prepare a potassium iodide solution by dis-

solving 35 grams in 100 c. c. of water and a mercuric chloride solution by dissolving 17 grams in 300 c. c. of water. Heat may be applied to aid the solution of the mercuric chloride, but the liquid must be cooled before use. The mercuric chloride solution is added to the potassium iodide solution until the precipitate of red mercuric iodide ceases to redissolve. The solution is then diluted to 1 liter with a 20 per cent solution of sodium hydroxide. Then add more of the mercuric chloride solution until a slight permanent precipitate again forms. Allow to stand and clear by settling, keeping it in a well-stoppered bottle and drawing off small quantities into another bottle from time to time as required for the tests. The reagent should have a light-yellow color. If it be colorless, more mercuric chloride must be added. Its sensitiveness should be tested from time to time with a very dilute solution of ammonium chloride.

4. *Standard ammonium chloride solution.*—Dissolve 0.7405 gram of pure ammonium chloride in ammonia-free water and dilute to 1 liter. Dilute 10 c. c. of this stronger solution to 500 c. c. This constitutes the standard ammonium chloride solution, and each cubic centimeter contains 0.005 milligram of NH_4.

5. *Standard colorimetric solution.*—This may be prepared by diluting 10 c. c. of the standard ammonium chloride solution (4) to about 90 c. c., adding 4 c. c. of the Nessler reagent (3), and diluting to 100 c. c. This standard should be prepared simultaneously with the development of the color in the solutions to be tested. This colorimetric standard contains 0.5 part of NH_4 per million.

Standards of other strengths can be similarly prepared when necessary, using, however, the same amount of Nessler reagent in the 100 c. c. of colorimetric solution.

Analytical process.

If the solution be colorless and free from salts which interfere with the reagents, the determinations can be made without previous distillation; otherwise it will be necessary to distill a measured quantity of the solution after it has been made alkaline with sodium carbonate. The flask and condenser should be rinsed with ammonia-free water. The condenser must be kept quite cold with the end dipping into a little ammonia-free water at the start. The distillate is made up to a definite volume. The distillation also has the advantage of concentrating the ammonia in the case of very weak solutions.

First test a small amount of the solution to ascertain the dilution necessary in order to get a good color for comparison. This may be done by adding some of the Nessler reagent (3) to a few cubic centimeters of the solution in a test tube. If a precipitate forms it will be necessary to dilute the solution and again test a small sample. The color of the solution should be a light shade of pure yellow. If

it has a deep yellow or reddish tint it is too strong to be used direct, and the amount to be used in 50 c. c. is approximately determined.

For the determination of the ammonia the volume of the solution determined approximately by the above test, is diluted to about 45 c. c., and 2 c. c. of Nessler reagent (3) are added, and then sufficient water to make 50 c. c. The standard colorimetric solution is prepared at the same time, and after fifteen minutes the comparison is made in the colorimeter or by one of the other colorimetric procedures.

Potassium I.

An indirect colorimetric method for the determination of potassium has been described by Cameron and Failyer [a] based on the red color produced by the addition of an excess of potassium iodide to a solution of a platinic salt, as described by Morrell.[b] The method consists in precipitating the potassium as chlorplatinate, after removing ammonia by ignition, and washing this with alcohol in a manner similar to that followed in the usual gravimetric procedure. The chlorplatinate is dissolved in water, and the addition of potassium iodide develops the red color above mentioned. The solution is then compared with a standard solution of potassium chlorplatinate in which the color has been similarly developed.

Since ammonium gives a precipitate analogous to the potassium chlorplatinate, it is highly essential to exclude it from all reagents used in the precipitation and washing of the potassium chlorplatinate as well as to exclude its presence in the air of the laboratory during this part of the manipulation.

Reagents required.

1. *Dilute sulphuric acid.*—Reagent.

2. *Hydrochloric acid.* — Equal volumes of concentrated hydrochloric acid and of water.

3. *Platinum chloride solution.*—Dissolve 1.73 grams of platinum chloride in 25 c. c. of water.

4. *Alcohol.*—Ninety-five per cent.

5. *Potassium iodide solution.* — Dissolve 25 grams of potassium iodide in water and dilute to 100 c. c.

6. *Standard potassium chlorplatinate solution.* — Dissolve 0.0621 gram of carefully recrystallized potassium chlorplatinate, K_2PtCl_6, in water and dilute to 1 liter. Each cubic centimeter contains 0.01 milligram of K.

7. *Standard colorimetric solution.*—This is prepared by diluting 10 c. c. of the standard potassium chlorplatinate solution (6) to about

[a] Jour. Amer. Chem. Soc., **25**, 1063 (1903).
[b] Jour. Amer. Chem. Soc., **2**, 145 (1880).

30 c. c., and then adding 1 drop of the hydrochloric acid (2) and 0.5 c. c. of the potassium iodide solution (5). Allow to stand at least an hour for the color to develop fully and then dilute to 100 c. c. This standard colorimetric solution has the strength of 1 part of K per million. The color should be developed in this standard at the same time that the colors are developed in the test solutions.

8. *Purified asbestos.*—A fine quality of fibrous hornblende asbestos is digested with hydrochloric acid and thoroughly washed. It is then ignited in a platinum dish to remove all traces of ammonium salts and is kept in alcohol free from ammonia in a tightly stoppered bottle. Instead of the asbestos small filter papers may be used, but great care must be taken to wash them absolutely free from ammonia.

Analytical process.

To a measured quantity of the solution to be determined, usually 50 c. c., contained in a porcelain dish, add about 0.5 c. c. of the dilute sulphuric acid (1). Evaporate to dryness on a water or steam bath and then drive off all excess of sulphuric acid and ammonium salts by heating over a naked flame, gently at first to avoid spattering, then strongly so as to destroy all organic matter. All subsequent operations up to the completion of the washing must be done in the complete absence of ammonia. To the cooled dish add a few drops of the hydrochloric acid (2) and several drops of platinum chloride solution (3), sufficient to give a slight excess of this reagent. The amount required will vary with the quantity of residue, but can be readily gauged after a little practice with the method. The residue is well worked up with the rounded end of a short stirring rod, and the solution evaporated on a water or steam bath almost to dryness. The stirring rod is allowed to stay in the dish during this and all subsequent procedures. Immediately on removing the dish from the water bath about 5 c. c. of alcohol (4) are put on the residue from a wash bottle, carefully washing down the sides of the dish and the stirring rod. Into a small Gooch crucible pour a sufficient amount of the alcohol suspension of purified asbestos (8) to make a thin but uniform and firm filter mat. When the alcohol has run through connect the filter in the usual manner with a suction pump. Only a very slight suction must be used. The contents of the porcelain dish are now poured gently into the filter, making no attempt to transfer the solid residue. This is again washed with about 3 c. c. of alcohol from the wash bottle, rinsing the dish and rod as before, and also the filter when pouring the liquid through it. Repeat this rinsing operation of dish and filter with four further portions of 3 c. c. each, and finally rinse the filter with about 5 c. c. of alcohol direct from the wash bottle. The dish and filter are then allowed to dry.

After the filter is dry, dissolve the precipitated potassium chlorplatinate with hot water by adding successive small portions to the dish, rinsing well the sides and rod and pouring through the filter, proceeding in general as with the washing operations described above, until approximately 25 c. c. of filtrate have been obtained. Cool the filtrate and add 1 drop of the hydrochloric acid (2) and 0.5 c. c. of the potassium iodide solution (5). Develop the color of the standard colorimetric solution (7) at the same time, as described above. After standing at least one hour the solution to be tested is diluted to 50 c. c., and the standard colorimetric solution to 100 c. c., and their relative strengths compared in the colorimeter. If the solution is much stronger than the standard it may be diluted to 100 c. c. or an aliquot portion taken and diluted to 100 c. c., the latter solution then being measured against the standard. If the solution is much weaker than the standard, the strength of the latter should be reduced by dilution.

Potassium II.

Hill [a] quite independently devised a similar method, but develops a yellow color instead of the red color of the preceding method. The procedure described by Hill is practically the same as far as the precipitation and washing of the chlorplatinate is concerned. The yellow color is produced by reduction of the potassium chlorplatinate with stannous chloride in the presence of free hydrochloric acid.

Reagents required.

In addition to the reagents numbered 1, 2, 3, 6, and 8, the following will be required:

9. *Alcohol.*—Eighty per cent.

10. *Stannous chloride solution.*—Boil 75 grams of powdered or granulated tin with 400 c. c. of concentrated hydrochloric acid in a flask until nearly all of the tin is dissolved. Keep in a tightly stoppered bottle over a small piece of tin.

11. *Standard colorimetric solution.*—As the yellow color developed in this method is less intense than the red color of the preceding method, it will be desirable to use a stronger colorimetric solution. This may be prepared by diluting 50 c. c. of the standard potassium chlorplatinate solution (6) to about 90 c. c., adding 6 c. c. of the stannous chloride solution (10) and making up to 100 c. c. This standard colorimetric solution has the strength of 5 parts of K per million. The color in this standard should be developed at the same time as that in the test solutions. Standard colorimetric solutions of other strengths may be prepared when necessary, but it will

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[a] Jour. Amer. Chem. Soc., **25**, 990 (1903).

be desirable always to have 6 c. c. of the stannous chloride solution in every 100 c. c. of colorimetric solution.

Analytical process.

The method consists in evaporating the solution to be tested, igniting the residue, precipitating, washing, and dissolving the potassium chlorplatinate, as in the preceding method, except that Hill uses 80 per cent alcohol for washing. The solution of the potassium chlorplatinate is diluted to about 45 c. c., and 3 c. c. of the stannous chloride solution (10) added and immediately made up to 50 c. c. The colorimetric standard solution is made up at the same time, and their relative strengths may be determined in the colorimeter as in the above method. Hill did not use a colorimeter in his work, but determined the strengths by direct comparison in the ordinary Nessler tubes.

Magnesium.[a]

An indirect colorimetric method for the determination of magnesium has been described by Schreiner and Ferris.[b] The method consists in precipitating the calcium as oxalate and converting the magnesium into ammonium magnesium phosphate as in the usual gravimetric method, all silica and excess of reagents being removed by washing with ammonia water. The ammonium magnesium phosphate is then dissolved in nitric acid and the magnesium determined indirectly by means of the well-known color produced by the action of molybdates on phosphates. Since silica gives a color similar to that of the phosphates it is imperative that it be excluded from the water and reagents used subsequently to the washing of the ammonium magnesium phosphate.

Reagents required.

1. *Silica-free water.*—Ordinary distilled water kept in glass is unsuitable for obtaining accurate results with this method. The water should be tested with the reagents described below and, if necessary, redistilled and kept in metallic containers.

2. *Ammonium hydroxide.*—Reagent.

3. *Ammonium oxalate solution.*—Saturated.

4. *Phosphate reagent.*—Dissolve 17.4 grams of potassium phosphate, K_2HPO_4, and 10 grams of ammonium chloride, NH_4Cl, in about 900 c. c. of water, add 50 c. c. of strong ammonium hydroxide solution (sp. gr. 0.9), and dilute to 1 liter. One cubic centimeter of this solution will precipitate 2.4 milligrams of magnesium.

5. *Ammonium hydroxide wash liquid.*—One volume of strong ammonium hydroxide solution (sp. gr. 0.9) and 9 volumes of water.

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[a] See also the titration method for magnesium.

[b] Jour. Amer. Chem. Soc., **26**, 961 (1904).

This liquid should be practically free from silica, and for this reason is best prepared by redistilling the ammonia into the water.

6. *Nitric acid.*—Specific gravity, 1.07.

7. *Ammonium molybdate solution.*—Dissolve 50 grams of pure ammonium molybdate in silica-free water, filtering if necessary, and dilute to 1 liter. The solution is preferably kept in a paraffin bottle to prevent contamination by the silica from glass (see page 20).

8. *Standard phosphate solution.*—Dissolve 0.3771 grams of pure, freshly crystallized sodium phosphate, $Na_2HPO_4.12H_2O$, in silica-free water and dilute to 1 liter. This standard solution should be kept in a paraffin or rubber bottle. Each cubic centimeter of this solution contains 0.1 milligram of PO_4.

9. *Standard colorimetric solution.*—This is prepared by diluting 10 c. c. of the standard phosphate solution (8) to about 80 c. c. with silica-free water and then adding 10 c. c. of the nitric acid (6) and 8 c. c. of the ammonium molybdate solution (7) and making up to 100 c. c. After standing twenty minutes it is ready for use. This standard colorimetric solution has a strength of 10 parts of PO_4, corresponding to 2.56 parts of Mg per million.

10. *Filter paper.*—This must be free from silica. Schleicher and Schüll's No. 589 or 590, 5 cm., has been used in this work.

Analytical process.

Measure out a convenient volume of the solution to be estimated, usually 50 c. c., into an evaporating dish, add 1 drop of ammonium hydroxide solution (2) and 2 or 3 drops of the ammonium oxalate solution (3); evaporate to dryness on a water bath. To the cooled dish add 1 c. c. of the phosphate reagent (4), work up the residue well with a glass rod, and allow to stand about two hours. The stirring rod is allowed to stay in the dish during this and all subsequent procedures. The precipitated magnesium ammonium phosphate is then washed as follows: Add about 5 c. c. of the ammonium hydroxide wash liquid (5) to the dish, washing down the sides, and pour the liquid through a small filter paper (10). Repeat this operation five times and continue washing down the filter and funnel until the filtrate measures approximately 50 c. c. Rinse the dish once with about 5 c. c. of cold water and pour through the filter in such a way as to wash the filter. Reject the washings and put a clean salt-mouth bottle or other receptacle under the funnel. Add 5 c. c. of the nitric acid (6) to the dish, work this about with the glass rod, and pour through the funnel in such a manner as to wet all the inside of the funnel. Wash the dish five times with hot silica-free water (about 5 c. c. each) and continue washing the filter until about 40 c. c. of the filtrate have been obtained. To the cooled liquid add 4 c. c. of the ammonium molybdate

solution (7), make up to 50 c. c., and after twenty minutes read against the standard colorimetric solution (9).

When the color developed is too strong for direct comparison with the standard solution an aliquot part is read. Great care must be taken to insure a sufficient amount of the reagents when dealing with comparatively large amounts of magnesium. The amounts of nitric acid (5 c. c.) and ammonium molybate solution (4 c. c.) given above are safe only up to about 0.3 milligram of magnesium in the 50 c. c. of colorimetric solution, or 6 parts per million. Should a considerable amount of magnesium be indicated by the amount of the magnesium ammonium phosphate precipitate or the color produced, it will be necessary to add a second portion of these reagents in order to develop the full color, diluting at the same time with silica-free water in such a manner as to keep the concentration of the reagents the same, namely, 5 c. c. of nitric acid and 4 c. c. of ammonium molybate solution in every 50 c. c. of the solution. With smaller amounts of magnesium, where the coloration to be compared is slight, it will be found very convenient and much more satisfactory to use for comparison a standard of only half the above strength.

Manganese.

Pichard,[a] Lemaire,[b] and others have determined small quantities of manganese in soils and plants by a colorimetric method. The manganese is oxidized to permanganate by means of peroxide of lead and nitric acid and compared with a standard solution of potassium permanganate. The method was first suggested by Pichard,[c] and is essentially that of Peters.[d] The directions below are those given by Clennell.[e] The method can be used only in the absence of chlorine.

Dr. W. F. Hillebrand, of the U. S. Geological Survey, has suggested to us the application of the persulphate method for the determination of manganese in soils. The method differs from the lead peroxide method here described in the use of potassium or ammonium persulphate and nitrate of silver as oxidizing agents for converting the manganese into permanganic acid. In the absence of chlorine no filtration or settling is necessary with the use of these reagents; in the presence of chlorine the method is available after filtering off the precipitated silver chloride. The method was first suggested by Marshall [f] and further studied and applied by Walters [g] to the determination of manganese in steels.

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a Compt. rend., **126**, 550 (1898).

b Bul. Soc. d. Pharm. de Bordeaux, Sept., 1897; Chem. News, **76**, 219 (1897).

c Compt. rend., **75**, 1821 (1872).

d Chem. News, **33**, 35 (1876).

e Eng. and Min. Jour., **78**, 827 (1904).

f Chem. News, **83**, 76 (1901).

g Chem. News, **84**, 239 (1901).

Dufty [a] has used sodium bismuthate as oxidizing agent for converting manganese into permanganic acid for its colorimetric determination.

Reagents required.

1. *Lead peroxide.*—This can be readily prepared, if not on hand, by digesting red lead in dilute nitric acid and filtering. It must be free from manganese.

2. *Nitric acid.*—Concentrated.

3. *Standard potassium permanganate solution.*—Dissolve 0.1438 gram of pure potassium permanganate in water, add 10 c. c. of pure concentrated nitric acid, and dilute to 1 liter. Each cubic centimeter of this solution will contain 0.05 milligram of Mn. This solution does not keep well, and if only an occasional test is to be made it is best to prepare a new solution each time.

Analytical process.

To 100 c. c. of the solution to be determined add 10 c. c. of concentrated nitric acid (2). Heat to boiling and then add gradually 0.5 gram of lead peroxide (1); continue the boiling for some minutes; allow to settle and cool. The solution is again made up to 100 c. c. with distilled water recently boiled and cooled. Stir well and filter through a small paper, rejecting the first portions of the filtrate. A definite volume of the filtrate, the quantity depending on the intensity of color, is put into a colorimetric tube. To distilled water contained in a similar tube there is added drop by drop the standard potassium permanganate solution (3), contained in a burette, until the tints of the two liquids appear identical.

A blank test should always be made, using the same quantities of nitric acid, water, lead peroxide, etc., as in the actual determination, for the success of the method depends upon the purity of the reagents used. The filtrate from the blank test should be colorless, indicating the absence of manganese, but it should give a tint, permanent for at least five minutes, on adding 1 c. c. of the permanganate solution, indicating the absence of reducing substances in the reagents.

Ordinary filter papers have a slight action on the permanganate, but according to Clennell this does not materially affect the result if the test be carried out as described, rejecting the first part of the filtrate. It would seem advisable, however, to substitute a good mat of asbestos for the filter paper, as described in the colorimetric potassium method.

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a Chem. News, **84**, 248 (1901).

Iron.

Iron may be detected and determined colorimetrically by means of the well-known blood-red color produced by sulphocyanates, due to the formation of ferric sulphocyanate. All ferrous compounds must be oxidized to the ferric condition. The method is that devised by Thomson [a] and described by Sutton.[b] It may also be determined colorimetrically by means of the blue color produced by potassium ferrocyanide,[c] or by using the very sensitive method described by Pulsifer,[d] based on the red color produced by the action of acetyl acetone on ferric salts.

Reagents required.

1. *Potassium sulphocyanate solution.*—Dissolve 10 grams of pure potassium sulphocyanate in water and dilute to 100 c. c.

2. *Diluted nitric acid.*—Dilute 30 c. c. of concentrated nitric acid to 100 c. c.

3. *Standard iron solution.*—Dissolve 0.3502 gram of pure recrystallized ammonium ferrous sulphate, $(NH_4)_2Fe(SO_4)_2 6H_2O$, in water, acidify with sulphuric acid, and oxidize the ferrous to the ferric salt by adding just sufficient potassium permanganate solution, and dilute to 500 c. c. Dilute 100 c. c. of this solution to 1 liter. This dilute solution constitutes the standard, and each cubic centimeter contains 0.01 milligram of Fe.

4. *Standard colorimetric solution.*—This may be prepared by diluting 10 c. c. of the standard iron solution (3) to about 80 c. c., adding 5 c. c. of the diluted nitric acid (2) and 5 c. c. of the potassium sulphocyanate solution (1), then making up to 100 c. c. This colorimetric standard contains 1 part Fe per million. Standards of other strengths can be prepared when necessary by varying the amount of standard iron solution and keeping the other reagents the same.

Analytical process.

A measured portion of the solution is evaporated to small bulk and treated with 2.5 c. c. of the dilute nitric acid and just sufficient permanganate solution to oxidize all the iron to the ferric condition. Dilute to about 40 c. c., add 2.5 c. c. of the potassium sulphocyanate solution (1), and make up to 50 c. c. Prepare a standard colorimetric solution of similar strength at the same time, and make the comparison in the colorimeter or by one of the other colorimetric procedures.

[a] Jour. Chem. Soc., **47**, 493 (1885).

[b] Volumetric Analysis, 9th ed., p. 227.

[c] Carnelly, Chem. News, **30**, 257 (1874) ; Bell, Jour. Soc. Chem. Ind., **8**, 175 (1889).

[d] Jour. Amer. Chem. Soc., **26**, 967 (1904). This article contains a bibliography of colorimetric methods and tests for iron.

Titanium.

Titanium can be very accurately determined by means of a colorimetric method proposed by Weller.[a]   Dunnington [b] has applied it to the determination of titanium in soils, and it has also become the most reliable method for the determination of this element in mineralogical work.[c]

The method consists in adding to the solution to be determined, which should contain at least 5 per cent of sulphuric acid, 1 or 2 cubic centimeters of hydrogen peroxide. The yellow color developed is then compared with a standard solution of titanium sulphate similarly treated. According to Hillebrand the colorimetric method gives results which are fully equal to those of the best gravimetric method. For the preparation of the solution for determining the titanium in soils and minerals see the articles cited above.

Nitrate.

The nitrates are best determined by means of the color produced by the action of phenoldisulphonic acid and making alkaline with ammonia. This method originated with Sprengel [d] and has been modified and improved by many subsequent investigators. The directions here given are essentially those of Gill,[e] who first gave definite directions for the preparation of the important reagent, the phenoldisulphonic acid. The nature of the compound resulting from the action of the nitrate upon this reagent is still a matter of dispute, but it is quite certain that it is not picric acid, as stated by Sprengel and as usually stated in the text-books. According to Montenari [f] it is dinitrophenol, but Andrews [g] finds it to be nitrophenolsulphonic acid. It is highly probable that these different results are due to the varying constitution of the reagents used, resulting from different methods of preparation and time of keeping.

Chlorides when present in considerable quantities interfere quite markedly with the determination of nitrates and must be previously removed. This is best accomplished by means of silver sulphate free from nitrates. This can be added in the solid form, thus avoiding dilution of the original solution. The silver sulphate is teste !

[a] Ber. deutsch. chem. Gesell., 15, 2592 (1882).

[b] Proc. Amer. Assoc. Adv. Science, 34, 132 (1885) ; Amer. Chem. Jour., 10, 36 (1889) ; Amer. Jour. Science, 42, 491 (1891) ; Jour. Amer. Chem. Soc., 13, 210 (1891) ; Chem. News, 76, 221 (1897).   See also Pellet and Fribourg, Jour. Chem. Soc., 88, II, 862 (1905).

[c] See Hillebrand, Bul. No. 176, p. 67, U. S. Geol. Survey, 1900 ; Noyes, Jour. Anal. and Appl. Chem. 5, 39 (1891).

[d] Poggendorff's Annalen, 121, 188 (1863).

[e] Technology Quarterly, 7, 55 (1894) ; Jour. Amer. Chem. Soc., 16, 122, 193 (1894).

[f] Gazz. chim. ital., 32–1, 87 (1902).

[g] Jour. Amer. Chem. Soc., 26, 388 (1904).

for nitrates by treating some of the solid salt with the phenoldisulphonic acid reagent, diluting with water and adding ammonia water. No yellow color should be produced. The silver sulphate as found in the market frequently contains nitrates in amounts sufficient to vitiate all results, and it is therefore advisable to prepare it specially for this work.

The presence of some kinds of organic matter also interferes seriously with the determination of nitrates by this method. In some cases it is the foreign color only which is produced by the strong acid, but often the action is of more vital importance, as a considerable loss of nitrates occurs, possibly due to oxidation of the organic matter by the nitrate instead of nitration of the phenoldisulphonic acid. In some cases it is advisable to reduce the nitrates to ammonia by means of the copper-zinc couple.[a] The ammonia is distilled off and determined colorimetrically. The ammonia originally present in the solution must be determined separately and deducted. Nitrites are likewise reduced to ammonia and must be allowed for, if present.

Reagents required.

1. *Phenoldisulphonic acid reagent.*—This is prepared by mixing 3 grams of pure crystallized phenol with 37 grams (20.1 c. c.) of concentrated sulphuric acid (sp. gr. 1.84) and heating for six hours at 100° C. by setting the lightly-stoppered flask in boiling water.

The acid thus prepared may crystallize out on standing, especially during the cold season. It may be brought into solution by heat, but the addition of water to effect solution is to be avoided.

2. *Ammonium hydroxide.*—Dilute strong ammonium hydroxide solution (sp. gr. 0.9) with an equal volume of water.

3. *Standard nitrate solution.*—Dissolve 0.1631 gram of pure, dry potassium nitrate in water and make up to 1 liter. Of this stronger solution 100 c. c. are diluted to 1 liter. This constitutes the standard nitrate solution and contains 0.01 of a milligram of NO_3 in each cubic centimeter.

4. *Standard colorimetric solution.*—Evaporate 10 c. c. of the standard nitrate solution (3) to dryness in a porcelain dish on a water or steam bath and treat as described under "Analytical process" below, finally diluting the solution to 100 c. c. This standard colorimetric solution has the strength of 1 part of NO_3 per million.

Analytical process.

Evaporate 50 c. c. or other convenient quantity, depending upon the amount of nitrate present, to dryness in a porcelain dish on a water bath, removing the dish as soon as it is completely dry. Add 1 c. c. of the phenoldisulphonic acid reagent (1) and stir thoroughly

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[a] See Sutton, Volumetric Analysis, 9th ed., p. 446; and also Wiley, Agricultural Analysis, I, p. 540, and other standard texts.

with the rounded end of a glass rod so as to loosen the residue and bring the acid well in contact with every portion of it. The time of action on the nitrate should be about ten minutes. At the end of this time the acid is diluted with about 15 c. c. of water and made alkaline with ammonium hydroxide (2), a yellow color being developed when the solution becomes alkaline. This is then diluted to 50 c. c. or 100 c. c. and compared with the standard colorimetric solution (4). If the color is too intense for direct comparison with this standard, an aliquot portion may be taken and diluted to definite volume and the strength of this determined.

Nitrite.

The nitrite is best determined by means of Ilosvay's [a] modification of Griess' [b] test, which has the advantage that the color is more rapidly developed and the reagents less liable to change. The red color produced is due to the action of the liberated nitrous acid on the sulphanilic acid, the resulting diazo-compound being in turn converted by the naphthylamine into azo-amidonaphthalenebenzenesulphonic acid.

Reagents required.

1. *Sulphanilic acid solution.*—Dissolve 0.5 gram of pure sulphanilic acid in 150 c. c. of dilute acetic acid (sp. gr. 1.04).

2. *Naphthylamine acetate solution.*—Boil 0.1 gram of α-naphthylamine in 20 c. c. of water and strain through a well-washed plug of absorbent cotton into 180 c. c. of dilute acetic acid (sp. gr. 1.04).

3. *Nitrite reagent.*—Mix equal volumes of the sulphanilic acid solution (1) and the naphthylamine acetate solution (2). This reagent is prepared from time to time in small quantities. If a reddish tint is developed on mixing the solutions it indicates the presence of nitrites. In this case the reagent is treated with zinc dust, which destroys the color, and after removing the excess of zinc it is ready for use.

4. *Standard sodium nitrite solution.*—Dissolve 0.0836 gram of pure silver nitrite in water. Add a solution of pure sodium chloride until silver chloride ceases to be precipitated. The volume is then made up to 250 c. c. and after thorough shaking allowed to stand in the dark until the precipitate has completely settled. Dilute 10 c. c. of the supernatant liquid to 100 c. c. with nitrite-free water. This standard must be kept in a well-stoppered bottle in the dark. Each cubic centimeter of this standard solution contains 0.01 milligram of NO_2.

The pure silver nitrite is prepared by adding to a hot concentrated solution of 16 parts of silver nitrate a hot concentrated solu-

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[a] Bul. Soc. Chim. (3), **2**, 347 (1889).
[b] Ber. d. deutsch. chem. Ges., **12**, 426 (1879).

tion of 10 parts of potassium nitrite. Allow to cool and separate the mother liquor by filtration with a filter pump. The silver nitrite is redissolved in the smallest possible quantity of hot water, allowed to cool, and the crystal mass again separated by means of suction. The crystals are then quickly dried in a water bath and preserved in a tightly stoppered bottle in the dark.

5. *Standard colorimetric solution.*—This may be prepared by diluting 10 c. c. of the above standard nitrite solution (4) to about 80 c. c., adding 16 c. c. of the nitrite reagent (3), and making up to 100 c. c. It must be prepared at the same time as the test solutions. This colorimetric standard has the strength of 1 part NO_2 per million, and solutions of other strengths may be similarly prepared when necessary, using the same quantity of reagent.

Analytical process.

Dilute a measured volume of the solution, if necessary, to about 40 c. c., add 8 c. c. of the nitrite reagent (3), and dilute to 50 c. c. Develop the color of the standard solution at the same time. Allow the solutions to stand fifteen minutes and then determine their relative strengths in the colorimeter or by direct comparison by any of the other colorimetric procedures.

Phosphate I.

During the past few years quite a number of procedures for the colorimetric estimation of phosphate have been devised, but nearly all have as a basis the development of the yellow color of the phosphomolybdates in acid solution. This coloration for the determination of phosphate has been used by Lepierre,[a] Jolles and Neurath,[b] and Jolles.[c] The phosphomolybdate coloration is influenced somewhat by the presence of large quantities of other salts, as shown by Veitch,[d] but the chief difficulty lies in the similar and even more intense coloration produced by the silicomolybdates. The chief aim in the various proposed procedures has been the elimination of the color produced by these silicomolybdates, either by removing the silica itself or by means of a differential coloration produced by varying the conditions.

Hewett[e] has devised an indirect colorimetric method for phosphates, applicable to larger quantities, by precipitating as phosphomolybdate and dissolving this in sodium hydroxide and saturating

[a] Bul. Soc. Chim. (3), **15**, 1213 (1896).

[b] Monatsh. Chem., **19**, 5 (1898).

[c] Arch. f. Hygiene, **34**, 22 (1899).

[d] Jour. Amer. Chem. Soc., **25**, 171 (1903). See also Smith, Jour. Amer. Chem. Soc., **26**, 897 (1904).

[e] Jour. Amer. Chem. Soc., **27**, 121 (1905).

the solution with hydrogen sulphide. The yellowish-red color produced is proportional to the phosphomolybdate present and is compared with a standard alkaline solution of phosphomolybdate similarly treated.

Schreiner and Brown [a] have described a method for the determination of small amounts of phosphates colorimetrically which gives good results. It consists in converting the phosphate into magnesium ammonium phosphate, as is done in the usual gravimetric procedure, all silica, as well as other salts, and to a large extent, also, soluble organic matter, being removed by washing with ammonia water. The magnesium ammonium phosphate is dissolved in nitric acid and determined by means of the yellow color produced by the addition of ammonium molybdate, comparing with a standard phosphate solution in which the color is similarly developed. The absence of silica in the water and reagents used subsequent to the washing of the magnesium ammonium phosphate must be assured.

Reagents required.

1. *Silica-free water.*—Ordinary distilled water kept or distilled in glass is unsuitable for obtaining accurate results with this method. The water should be tested with the reagents described below, and if necessary redistilled, using a metallic condenser and stored in metallic containers.

2. *Ammonium hydroxide.*—Reagent.

3. *Ammonium oxalate solution.*—Saturated.

4. *Magnesium reagent.*—Dissolve 13 grams of magnesium chloride, $MgCl_2.6H_2O$, and 20 grams of ammonium chloride, NH_4Cl, in about 900 c. c. of water, add 50 c. c. of strong ammonium hydroxide (sp. gr. 0.9), and dilute to 1 liter. One cubic centimeter of this solution will precipitate 6 milligrams of PO_4.

5. *Ammonium hydroxide wash liquid.*—One volume of strong ammonium hydroxide (sp. gr. 0.9) and 9 volumes of water. This liquid should be practically free from silica, and for this reason is best prepared by redistilling the ammonia into the water.

6. *Nitric acid.*—Specific gravity 1.07.

7. *Ammonium molybdate solution.*—Dissolve 50 grams of pure ammonium molybdate in silica-free water, filter if necessary, and dilute to 1 liter. The solution is preferably kept in a paraffin bottle to prevent contamination by the silica from glass (see page 20).

8. *Standard phosphate solution.*—Dissolve 0.3771 gram of pure, freshly crystallized sodium phosphate, $Na_2HPO_4.12H_2O$, in silica-free water and dilute to 1 liter. This standard solution should be kept in a paraffin or rubber bottle. Each cubic centimeter of this solution contains 0.1 milligram of PO_4.

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[a] Jour. Amer. Chem. Soc., **26**, 1463 (1904).

9. *Standard colorimetric solution.*—This is prepared by diluting 10 c. c. of the standard phosphate solution (8) to about 80 c. c. with silica-free water, and then adding 10 c. c. of the nitric acid (6) and 8 c. c. of the ammonium molybdate solution (7) and making up to 100 c. c. After standing twenty minutes it is ready for use. This standard colorimetric solution has a strength of 10 parts of PO_4 per million.

10. *Filter paper.*—This must be free from silica. Schleicher and Schüll's No. 589 or No. 590, 5 cm., has been used for this colorimetric work.

Analytical process.

Measure out a convenient volume of the solution to be estimated. usually 50 c. c., into an evaporating dish, add 1 drop of ammonium hydroxide (2), and 2 or 3 drops of the ammonium oxalate solution (3); evaporate to dryness on a water bath. To the cooled dish add 1 c. c. of the magnesium reagent (4), work up the residue well with a glass rod, and allow to stand about two hours. The stirring rod is allowed to stay in the dish during this and all subsequent procedures. The precipitated magnesium ammonium phosphate is washed as follows: Add about 5 c. c. of the ammonium hydroxide wash liquid (5) to the dish, washing down the sides, and pour the liquid through a small filter paper (10). Repeat this operation five times and continue washing down the filter and funnel until the filtrate measures approximately 50 c. c. Rinse the dish once with about 5 c. c. of cold water and pour through the filter in such a way as to wash the filter. Reject the washings and put a clean saltmouth bottle or other receptacle under the funnel. Add 5 c. c. of the nitric acid (6) to the dish, working this about with the glass rod, and pour through the funnel in such a manner as to wet all the inside of the funnel. Then wash the dish five times with hot silica-free water (about 5 c. c. each) and continue washing the filter until about 40 c. c. of the filtrate have been obtained. To the cooled liquid add 4 c. c. of the ammonium molybdate solution (7), make up to 50 c. c., and after twenty minutes read against the standard colorimetric solution (9).

When the color developed is too strong for direct comparison with the standard solution, an aliquot part is taken and diluted. Great care must be taken to insure a sufficient quantity of the molybdate reagents when dealing with comparatively large amounts of phosphates, as otherwise the full color will not be developed. Should a considerable quantity of phosphate be indicated by the quantity of the magnesium ammonium phosphate precipitate or the color produced, it will be necessary to add a second portion of these reagents in order to develop the full color, diluting at the same time with silica-free water in such a manner as to keep the concentration of the

reagents the same, namely, 5 c. c. of nitric acid and 4 c. c. of ammonium molybdate solution in every 50 c. c. of the solution. With the smaller quantities of phosphate, where the coloration to be compared is slight, it will be found very convenient and much more satisfactory to use for comparison a standard of only half the above strength.

Phosphate II.

Woodman and Cayvan [a] separate the silica by evaporating the solution with nitric acid and heating the residue for two hours in a water oven. They found that at 100° C. the silica is rendered completely insoluble, but if a temperature above or below this point be used a considerable amount of silica would again pass into solution. The residue is then treated with water and the dissolved phosphate determined by the color produced with ammonium molybdate. The method described below is essentially that of Woodman and Cayvan, but the proportion of reagents found by Veitch [b] to give the maximum coloration is used.

Reagents required.

The reagents numbered 1, 6, 7, 8, 9, and 10 of the preceding method will be required for this method.

Analytical process.

To a measured quantity of the solution to be tested 3 c. c. of the nitric acid (6) are added and the solution evaporated to dryness in a small porcelain dish on a water bath. The residue is then heated in an oven for two hours at the temperature of boiling water. The dry residue is then treated with several portions of cold silica-free water until about 40 c. c. of solution are obtained, filtering only if necessary. To this solution 5 c. c. of the nitric acid (6) and 4 c. c. of the ammonium molybdate solution (7) are added and made up to 50 c. c. The color in the standard solution (9) is developed at the same time, and after standing twenty minutes their relative strengths are determined.

Veitch has shown that when the amount of calcium and magnesium present is large it is advisable to evaporate the solution twice with the nitric acid, filtering between the evaporations. After heating at 100°C. for two hours 5 c. c. of the nitric acid are added to the residue. Filter and wash to about 45 c. c., and then add 4 c. c. of the ammonium molybdate solution, making up to 50 c. c.

Silica.

Since silica gives with molybdates a color almost identical with that produced by the phosphates, this color is measured simultane-

[a] Jour. Amer. Chem. Soc., 23, 96 (1901) ; 24, 735 (1902).
[b] Jour. Amer. Chem. Soc., 25, 169 (1903).

ously with that produced by the latter. The phosphate is determined in a separate portion and the difference is then wholly due to the color of the silicomolybdate produced. As the comparison is made with a standard phosphate solution, it is necessary to know the relative amounts of phosphates (PO_4) and silica (SiO_2) which will give an equal intensity of color. This ratio has been found to be 0.41 by Veitch[a] and 0.40 by Schreiner.[b]

Reagents required.

The same reagents as in the phosphate method will be required. The 10 parts PO_4 per million of the standard colorimetric solution (9) are the equivalent in color of 4 parts SiO_2 per million.

Analytical process.

Determination of the phosphate, A.—This is determined by either of the above methods and the result expressed in parts PO_4 per million of the original solution.

Determination of both silica and phosphate, B.—Dilute a measured volume, the quantity depending upon the strength of the solution, to about 40 c. c. with silica-free water, add 5 c. c. of the nitric acid (6) and 4 c. c. of the ammonium molybdate solution (7) and make up to 50 c. c. The color developed will be due to silica and to phosphate if the latter be present. After twenty minutes compare with the standard colorimetric phosphate solution (9), expressing the result as parts PO_4 per million of the original solution.

Calculation of the silica, x.—The result B is the sum of the phosphate A determined as above described and the silica x, the factor 0.4 being used to convert the silica into the equivalent amount of phosphate, since B is determined in terms of the phosphate standard. This relation is expressed by the equation

$$B = A + \left(\frac{x}{0.4}\right) \text{ whence } x = 0.4\,(B-A).$$

Therefore to get parts SiO_2 per million parts of the original solution subtract the phosphate result A from the silica and phosphate result B and multiply the difference by 0.4.

Silica and Phosphate.

That silica in solutions will give different intensities of coloration with molybdates under two different conditions, while phosphates give the same intensity of coloration under these two conditions, has been shown by Schreiner.[c] When, as is usually done in the colorimetric estimation of phosphates, the nitric acid and ammonium

[a] Jour. Amer. Chem. Soc., **25**, 179 (1903).
[b] Jour. Amer. Chem. Soc., **25**, 1059 (1903).
[c] Jour. Amer. Chem. Soc., **25**, 1056 (1903); **26**, 808 (1904).

molybdate solutions are added simultaneously to a silica solution, a certain intensity of color is developed. If, however, the ammonium molybdate reagent be added to the silica solution, and after a period of time the nitric acid, the intensity of color produced by the same quantity of silica will be far less than in the first case. Experiments have shown that the solution must stand at least one hour with the ammonium molybdate reagent before adding the nitric acid in order to get the maximum effect. Some color is developed by the ammonium molybdate alone, though this is greatly influenced by the presence of other salts, temperature, etc., but upon adding the nitric acid the color always comes up to a definite intensity. The ratio of the color produced by adding the reagents simultaneously to that produced by adding the nitric acid one hour after the ammonium molybdate, was found by Schreiner to be 0.49, or for practical purposes, 0.5, which value has been corroborated by Lincoln and Barker.[a]

On this different coloration produced by the action of ammonium molybdate on silica under conditions which produce no change in the effect of this reagent on phosphate has been based a method for determining the silica simultaneously with the phosphate. The measurements are made with the standard colorimetric phosphate solution as in the preceding methods, using the factor 0.4 for calculating the silica corresponding to the phosphate. If a portion of a solution containing both phosphate and silica be treated with ammonium molybdate reagent and nitric acid simultaneously a certain result, A, which is the sum of the effects produced by both phosphate and silica, will be obtained. This is represented by the equation

$$(1) \qquad A = y + \left(\frac{x}{0.4} \right)$$

where y is the amount of phosphate present and x the amount of silica present, the factor 0.4 being used to convert the silica into the equivalent amount of phosphate, since A is determined in terms of the phosphate standard. If a second portion of the same solution containing both phosphate and silica be treated with ammonium molybdate reagent and an hour later the nitric acid be added, a different result, B, will be obtained, the silica under this condition having only one-half as great an effect as before. This is represented by the equation

$$(2) \qquad B = y + 0.5 \left(\frac{x}{0.4} \right)$$

There are consequently two simple equations containing two unknown quantities which are, therefore, readily determined:

Subtracting equation (2) from equation (1) we get

$$A - B = 0.5 \left(\frac{x}{0.4} \right), \text{ or } x = 0.8 \, (A - B).$$

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[a] Jour. Amer. Chem. Soc., **26**, 975 (1904).

Subtracting equation (1) from twice equation (2) we get

$$y = 2B - A$$

Reagents required.

The reagents numbered 1, 6, 7, 8, and 9 of the phosphate method on page 43 will be required in this procedure. The 10 parts PO_4 per million of the standard colorimetric solution (9) are the equivalent in color of 4 parts SiO_2 per million.

Analytical process.

Determination of the A result.—Dilute if necessary a measured volume of the solution to be determined to about 40 c. c. with silica-free water, add 5 c. c. of the nitric acid (6) and 4 c. c. of the ammonium molybdate solution (7), and make up to 50 c. c. After twenty minutes the colorimetric reading is made against the standard colorimetric solution (9), expressing the result as parts PO_4 per million of the original solution.

Determination of the B result.—Dilute a second portion of the solution to about 40 c. c. and add 4 c. c. of the ammonium molybdate solution (7). Allow to stand one hour. At the end of this time add 5 c. c. of the nitric acid (6), and after twenty minutes make the color comparison against the standard (9) as above, again expressing the result as parts PO_4 per million of the original solution.

Calculation of the silica and the phosphate.—From the A and B results the silica and the phosphate present in the solution are readily calculated by means of the equations solved above.

To obtain the parts SiO_2 per million parts of solution, subtract B from A and multiply the difference by 0.8.

To obtain the parts PO_4 per million parts of solution, subtract A from twice B.

Example.—A 25 c. c. portion was diluted to 40 c. c., ammonium molybdate solution and nitric acid added and the volume made up to 50 c. c. Comparing in the colorimeter it was found that a height of 30 scale divisions corresponded to 34.5 scale divisions of the standard. This gives the strength of the colorimetric solution as $\frac{34.5}{30} \times 10 = 11.5$ and the strength of the original solution as $11.5 \times 2 = 23$, which is the A result.

A second portion of 25 c. c. was diluted to 40 c. c. and the ammonium molybdate solution added. After an hour the nitric acid was added and the volume made up to 50 c. c. Comparing in the colorimeter it was found that a height of 40 scale divisions corresponded to 26 scale divisions of the standard. This gives the strength of the colorimetric solution as $\frac{26}{40} \times 10 = 6.5$ and the strength of the original solution as $6.5 \times 2 = 13$, which is the B result.

The parts SiO_2 per million of solution will then be 0.8(23—13) or 8.

The parts PO_4 per million of solution will be (13×2)—23 or 3.

Lincoln and Barker [a] have suggested that where the proportion of phosphate to silica is very small, about 0.5 of a milligram of PO_4 (5 c. c. of the standard phosphate solution (8) given on p. 43) be added to each 50 c. c. of liquid in the above method, but otherwise proceeding as before. The result for the parts PO_4 per million of solution is corrected by subtracting the phosphate added, which is 10 parts PO_4 per million.

Sulphate. [b]

Winkler [c] has modified the procedure of Andrews [d] for the determination of sulphate, changing it at the same time into a colorimetric method suitable for determining small quantities. The method consists in treating the acidified solution to be examined with barium chromate, the insoluble barium sulphate being formed and upon neutralizing an amount of CrO_4 equivalent to the precipitated SO_4 remains in solution. After filtering, the color is compared with that of a standard solution of chromate. A correction must be made for the solubility of the barium chromate, which was determined by Winkler, for the conditions under which the method is used, to be 1 part of barium chromate in 46,400 parts of water.

The procedure as described by Winkler, who did not use a colorimeter, is given below, although this may be readily modified so that it can be used with the colorimeter.

Reagents required.

1. *Barium chromate.*—The pure barium chromate is prepared by adding a solution of potassium chromate to a hot solution of barium chloride, until the liquid above the precipitate of barium chromate appears yellow. The precipitate is first washed by decantation and then thoroughly on a filter, beginning with water slightly acidified with acetic acid. After drying it is rubbed to a powder.

2. *Hydrochloric acid.*—Concentrated.

3. *Sodium hydroxide solution.*—Reagent.

4. *Standard potassium dichromate solution.*—The potassium dichromate is purified by recrystallizing from a hot solution, stirring well while the crystals are forming. The crystal magma is drained and dried at 100–110° C.

[a] Jour. Amer. Chem. Soc., **26,** 975 (1904).
[b] See also the turbidity method for sulphate.
[c] Zeit. anal. Chem., **40,** 465 (1901).
[d] Amer. Chem. Jour., **11,** 567 (1890).

Of the pure salt 1.533 grams are dissolved in water and the solution diluted to 1 liter. The solution remains unchanged if kept in a glass-stoppered flask. Each cubic centimeter of this standard solution corresponds to 1 milligram of SO_4.

Analytical process.

To 150 to 200 c. c. of the solution to be tested, contained in a boiling flask, add 5 to 10 drops of concentrated hydrochloric acid (2), and sprinkle 0.1 to 0.2 gram of pure barium chromate (1) into the liquid. The liquid is now heated over a free flame and boiled for an instant. To the completely cooled liquid sodium hydroxide solution (3) is added until a drop of the liquid produces a faint blue color on red litmus paper. A greater excess of sodium hydroxide is to be avoided. The liquid is then poured through a double filter; the first portions, which are usually still cloudy, are discarded, the clear filtrate only being collected.

Of the clear filtrate 100 c. c. are put into a comparison cylinder, and 100 c. c. of water, to which are added a few drops of sodium hydroxide solution, are put into a similar cylinder. The standard potassium dichromate solution, contained in a burette, is now dropped into the latter cylinder until no difference in color is perceptible between the two solutions. For accurate measurements, especially when much potassium dichromate solution was used, the test solution is diluted with the corresponding volume of distilled water so as to have equal volumes of the solutions for comparison. Multiplying the number of cubic centimeters of the potassium dichromate solution required by 10 will give the number of milligrams per liter or parts SO_4 per million of solution. This figure must be corrected for the solubility of the barium chromate under these conditions. This has been found to be equivalent to 8.2 parts of SO_4 per million of solution, and the above results are therefore corrected by subtracting 8.2 from them.

Sulphide.

For the determination of hydrogen sulphide in natural waters the method of Dupasquier is usually recommended in text-books.[a] The amount of sulphide in ground waters is, however, often so small that it can no longer be determined by the above method. Its determination is sometimes of considerable interest in soil studies, as, for instance, in swampy places, due to the decomposition of iron pyrite, and in many of the drainage waters resulting from irrigation of "alkali" tracts where gypsum is present. In such waters hydrogen

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[a] Frezenius, Quant. Chem. Anal., 6th ed., vol. 1, p. 558.

sulphide is frequently found as the result of the decomposition of the gypsum by the thiobacteria, notably *Beggatoria alba*.

One of the colorimetric methods for the determination of sulphides consists in using the red color developed with sodium nitroprussiate in alkaline solution.[a]   The red color is compared with a standardized solution of hydrogen sulphide similarly treated, and according to Ohlmüller satisfactory results can be obtained by this method.

Winkler[b] has developed a colorimetric method for the determination of small quantities of hydrogen sulphide in natural waters by comparing the color developed in the water by the addition of an alkaline solution of lead acetate containing Rochelle salt (to prevent the separation of calcium and magnesium carbonate), with the color of a standard alkaline solution of arsenic trisulphide similarly treated.   According to Winkler, thiosulphate, if present in such waters, does not affect the result.

The procedure and reagents as used by Winkler are given below.

Reagents required.

1. *Alkaline lead acetate solution.*—Dissolve 25 grams of crystallized sodium potassium tartrate, 5 grams of sodium hydroxide, and 1 gram of lead acetate in water and make up to 100 c. c.

2. *Standard arsenic trisulphide solution.*—Prepare pure arsenic trisulphide by adding a solution of 1 gram of arsenic trioxide in dilute hydrochloric acid to 100 c. c. of fresh hydrogen sulphide water, washing the precipitate and drying at 100° C.

Dissolve 0.0366 gram of the pure dry arsenic trisulphide in a few drops of ammonia and dilute to 100 c. c.   This solution can not be kept on hand, as it changes rapidly, and is therefore prepared immediately before using.   Each cubic centimeter of this solution corresponds to 0.1 c. c. of hydrogen sulphide at 0° and 760 mm. pressure, or 0.143 milligram of S as sulphide.

Analytical process.

Pour 100 c. c. of the water to be tested into a colorimetric tube containing 5 c. c. of the alkaline lead acetate solution (1).   Into a similar tube are put 100 c. c. of distilled water and 5 c. c. of the reagent. The standard arsenic trisulphide solution (2), contained in a burette, is now dropped into the latter tube until both liquids are equally colored.   The volume of the standard solution required gives the number of cubic centimeters of hydrogen sulphide gas per liter of the solution, or when multiplied by 1.43 it gives the parts S as sulphide per million of solution.

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[a] Ohlmüller, Guide pratique pour l'analyse de l'eau, French translation by Gautier, p. 50.

[b] Zeit. anal. Chem., **40**, 772 (1901).

TURBIDITY METHODS.

The measurement of the turbidity of an unknown solution by comparison with the turbidity of a standard solution produced by the addition of barium chloride and ammonium oxalate, respectively, has been used in determining sulphate and calcium in soil solutions. In making the determinations it is desirable that the solutions be sufficiently dilute to insure an opalescence and not an actual settling out of the precipitate. It is, moreover, important that the standard and the unknown solution be not widely different in strength to insure a similar appearance of the opalescence, and it is therefore advisable to make a preliminary test in a test tube. If the unknown solution gives a much denser turbidity than the standard solution, it should first be diluted, as dilution subsequent to the precipitation will not give a satisfactory result. While it is possible to determine the turbidity, the tint will not correspond with that of the standard, and it will be difficult to make an accurate setting. Unfortunately the turbidity itself and quite markedly the tint of the turbidity are dependent on the conditions of precipitation, as these determine the size of the particles. This has been well pointed out by Richards and Wells[a] in connection with the precipitation of silver chloride, and the same principles apply in the other cases. The rate of precipitation and the tint of the opalescence are greatly influenced by the presence of other salts, and it is therefore difficult to prepare a standard which will behave in exactly the same way as the solution to be estimated. The addition of an excess of an electrolyte to both solutions induces equal speed of precipitation, and therefore insures a similar appearance to the turbidity. This precaution is observed in the methods described below.

The solid salts are added to avoid any further dilution in case the amounts present should be small. Such a procedure would cause a considerable occlusion of the salt by the precipitate in working with stronger solutions, but with the small amount of precipitate formed in the concentrations worked with this tendency is reduced to a minimum.

For making the comparisons the colorimeter described on page 22 is preferably used, as the movement of the reservoir up and down helps to keep the standard solution well stirred up from the bottom. The other colorimeter may also be used, but care must be taken to stir or shake the liquid thoroughly before each determination, if a series of solutions is under examination. The readings are made as with colorimetric solutions, comparing this time images of equal turbidity. With some practice fairly concordant results can be rapidly obtained. That very accurate results can be obtained in turbidity

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[a] Jour. Amer. Chem. Soc., **27**, 459 (1905).

measurements by taking proper precautions and making the readings in a specially constructed instrument called the nephelometer has been pointed out by Richards and Wells.[a] This procedure was used by them in the course of their work on the solubility of silver chloride and the revision of the atomic weights of sodium and chlorine.

The turbidity methods here described are adaptations of photometric methods to small quantities, the photometric methods requiring a larger amount of precipitate. In the photometric method the length of column of the turbid liquid is ascertained, which will just cause a small standard flame to become invisible.[b]

DESCRIPTION OF THE TURBIDITY METHODS

Calcium.[c]

Calcium can be determined with close approximation by the turbidity produced by the addition of ammonium oxalate. The photometric method of Hinds [d] was modified by Mr. W. S. Ferris, of this Bureau, so as to be applicable to small quantities. The conditions of precipitation in working with small quantities had to be studied closely, so as to insure complete precipitation of the calcium oxalate without the simultaneous precipitation or occlusion of magnesium oxalate. Richards, McCaffrey, and Bisbee [e] have shown in their study of this subject from a gravimetric point of view that while ammonium chloride prevents the precipitation of magnesium oxalate, it has at the same time a similar but less considerable effect on the calcium oxalate, thus necessitating the presence of a larger amount of ammonium oxalate to completely precipitate the calcium and yet hold all magnesium in solution. On the other hand, an undue excess of these salts must be avoided. The most effective concentration of ammonium chloride and ammonium oxalate to produce correct results in working with very small amounts of calcium was therefore determined, and these quantities are given in the following description of the method:

Reagents required.

1. *Ammonium oxalate, powdered.*—The salt must give a clear solution in water. For measuring the ammonium oxalate a glass tube is fused at one end and cut so as to make a little cup which holds 0.2 gram of the powder.

2. *Ammonium chloride, powdered.*—The salt must give a clear solution in water. Make a little glass cup, as described above, which will hold 0.4 gram of the powder.

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[a] Amer. Chem. Jour., **31**, 235 (1904) ; Jour. Amer. Chem. Soc., **27**, 459 (1905).

[b] See Hinds, Jour. Amer. Chem. Soc., **18**, 661 (1896) ; also Leighton, Field Assay of Water, U. S. Geol. Survey, 1905.

[c] See also the titration method for calcium.

[d] Jour. Amer. Chem. Soc., **18**, 661 (1896) ; **22**, 269 (1900).

[e] Proc. Amer. Acad., **36**, 377 (1900–1).

3. *Standard calcium solution.*—Dilute a strong analyzed solution of calcium chloride, so that the solution will contain 0.1 milligram of Ca per cubic centimeter.

4. *Standard turbidity solution.*—Dilute 50 c. c. of the standard calcium solution (3) to 1 liter. Of this dilute solution use 100 c. c. and put into a glass-stoppered bottle in series with the solutions to be tested. At the same time that the solutions are treated with reagents add 0.4 gram (2 measures) of ammonium oxalate (1) and 0.8 gram (2 measures) of ammonium chloride (2). Each cubic centimeter of this standard turbidity solution contains 0.005 milligram of Ca— i. e., it has a strength of 5 parts of Ca per million of solution.

Analytical process.

Measure out 50 c. c. of the solution to be tested (less if rich in calcium, always diluting, however, up to 50 c. c. before adding the reagents) into a glass-stoppered bottle and add 0.4 gram (1 measure) of ammonium chloride, and allow to dissolve. Then add 0.2 gram (1 measure) of ammonium oxalate and agitate occasionally until the salt has dissolved. Allow to react at least one hour before reading. The standard turbidity solution is prepared at the same time, and the relative turbidities of the liquids then compared in the colorimeter.

Sulphate.[a]

For the determination of sulphate the turbidity produced by the addition of barium chloride gives a close approximation. The method is a modification by Mr. J. O. Belz of this Bureau of the photometric procedure of Hinds [b] and Jackson,[c] and instead of reading the depth of turbid liquid at which a standard flame just ceases to be visible, the turbidity of the test solution is compared in the colorimeter with a standard turbidity solution.

Reagents required.

1. *Barium chloride.*—Powdered or in small crystals.

2. *Hydrochloric acid.*—Concentrated.

3. *Standard potassium sulphate solution.*—Dissolve 0.9071 gram of pure potassium sulphate in water and dilute to 1 liter. Each cubic centimeter of this solution contains 0.5 milligram of SO_4.

4. *Standard turbidity solution.*—Dilute 20 c. c. of the standard sulphate solution to 1 liter. Of this dilute solution use 100 c. c. and put into series with the test solutions, treating it in every way as described below under "Analytical process" at the same time that the

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[a] See also the colorimetric method for sulphate.

[b] Jour. Amer. Chem. Soc., **18**, 661 (1896) ; **22**, 269 (1900).

[c] Jour. Amer. Chem. Soc., **23**, 799 (1901) ; see also Leighton, Field Assay of Water, U. S. Geol. Survey, 1905.

test solutions are being precipitated. Each cubic centimeter of this standard turbidity solution contains 0.01 milligram of SO_4—i. e., it has a strength of 10 parts SO_4 per million of solution.

Analytical process.

Measure out 50 c. c. of the solution to be tested (less, if rich in sulphate, always diluting, however, up to 50 c. c. before adding the reagents) into a tightly glass-stoppered saltmouth bottle. Acidify the solution by adding one or two drops of hydrochloric acid (2), and, finally, add about 0.1 to 0.2 gram of solid barium chloride (1). Shake vigorously at intervals during thirty to forty minutes. The standard turbidity solution (4) is prepared at the same time and the liquids are then compared in the colorimeter.

Chloride.[a]

Richards and Wells [b] have devised a very accurate nephelometric process for the determination of minute quantities of chlorides or of silver. The method for chloride consists in adding an excess of silver nitrate to the solution to be determined and to a solution of known strength used as a standard. The relative turbidities of the two liquids are then determined in the improved nephelometer described by Richards and Wells in the first article cited above. According to the authors, the method is to be ranked among those suitable for exact work, as the degree of accuracy is as great as can be attained in the collection of a precipitate for weighing.

TITRATION METHODS.

The exact determination of the end point in the titration of very dilute solutions, with a dilute standard solution, can only be satisfactorily accomplished by comparison with a second tube of distilled water or solution to which the same amount of indicator has been added as was put into the solution being titrated. The slightest change in the color or tint of the solution being titrated is thus made perceptible.

The burettes used in the titration of carbonate, bicarbonate, and chloride are of very narrow bore and graduated into fiftieths of a cubic centimeter. For convenience in dropping, the end of the glass stopcock is drawn out to a point and this broken off until the burette delivers 50 drops to the cubic centimeter. As the capacity of the burette is necessarily small, it should be connected directly with a larger bottle serving as reservoir.

[a] See also the titration method for chloride.

[b] Amer. Chem. Jour., **31**, 235 (1904) ; Jour. Amer. Chem. Soc., **27**, 459 (1905).

DESCRIPTION OF THE TITRATION METHODS.

Calcium.[a]

The calcium can be determined by the well-known soap method of Clarke, as modified by Winkler.[b] The method gives fairly good results, but when a comparatively large amount of magnesium is present the determination is less satisfactory, as already pointed out by Grittner.[c] Some interesting observations on the action of soap on calcium and magnesium solutions have also been made by Gott-schalk and Roesler.[d]

The factor for the potassium oleate solution varies somewhat with different concentrations in calcium, and it is therefore advisable to dilute the unknown solution so that it has approximately the strength of the calcium solution used in standardizing the potassium oleate solution, or else to determine the factor for several different strengths of the standard solution.

Walker[e] has made some suggestions for the determination of " hardness " in waters when the concentration is greater than 40 parts calcium per million.

Reagents required.

1. *Standard potassium oleate solution*.—Dissolve 15 c. c. of pure oleic acid in 600 c. c. of alcohol and add 4 grams of potassium hydroxide dissolved in 400 c. c. of water. Shake occasionally during the first day and allow to stand for two or three days until clear. Carefully pour through a filter paper. Of this stronger solution 250 c. c. are diluted to 1 liter with a mixture of 6 volumes of alcohol and 4 volumes of water. Each cubic centimeter of this solution will precipitate approximately 0.2 milligram of calcium, but its exact equivalence must be determined by using 50 c. c. of the standard calcium solution (2), proceeding exactly as described under "Analytical process."

2. *Standard calcium solution*.—Dilute a standardized calcium chloride solution so that each cubic centimeter will contain 0.02 milligram of Ca.

This may also be prepared by dissolving cautiously 0.2498 gram of pure Iceland spar in a little hydrochloric acid, evaporating to remove excess of acid and diluting to 500 c. c. Of this solution 100 c. c. are again diluted to 1 liter to get the standard strength of 0.02 milligram per cubic centimeter.

3. *Alkaline tartrate solution*.—Dissolve 6 grams of potassium hy-

[a] See also the turbidity method for calcium.

[b] Zeit. anal. Chem., **40**, 82 (1901).

[c] Zeit. angew. Chem., **15**, 847 (1902).

[d] Jour. Amer. Chem. Soc., **26**, 851 (1904).

[e] Technology Quarterly, **17**, 281 (1904).

droxide and 100 grams of sodium potassium tartrate in 500 c. c. of water.

To test the purity of this reagent 0.1 c. c. of the potassium oleate solution is added to 5 c. c. of the reagent, diluted to 50 c. c.; after shaking for fifteen seconds a foam permanent for 1 minute should be produced.

Analytical process.

A measured portion of the solution to be tested, the quantity depending upon the concentration in calcium, is diluted to approximately 50 c. c. in a cylindrical bottle, which can be closely stoppered, and 3 c. c. of the alkaline tartrate solution (3) added. The potassium oleate solution (1) is then added cautiously from a glass-stoppered burette. The bottle is vigorously shaken for fifteen seconds after each addition and placed on its side, and the length of time it takes for the foam to break is noted. When the foam persists all over the surface for two minutes the reaction is complete. The end reaction can be quite sharply determined after some preliminary practice. The method gives very sharp end results when the proportion of magnesium to calcium is small, but when the amount of magnesium is large the sensitiveness of the method is much interfered with. From the volume of oleate solution required and the volume of the original solution the strength of the latter is calculated. If more than 10 c. c. of the oleate solution are required it is advisable to repeat the operation with a smaller quantity, always, however, diluting to 50 c. c. "False" foaming is sometimes noticed at the very start, and it is therefore advisable to wait until the false foam has broken. After breaking, the reaction goes on smoothly to the end.

Magnesium.[a]

The magnesium may be determined by using Winkler's modification of the calcium method described above. An alkaline ammonium chloride solution containing 10 grams of the salt and 35 c. c. of concentrated ammonium hydroxide in 500 c. c. is used in place of the alkaline tartrate solution. The titration is made as described in the last method. The magnesium reacts more slowly and less satisfactorily than calcium and has a tendency to produce "false" foaming at the very start of the reaction. In this titration both the calcium and the magnesium react with potassium oleate. The calcium is therefore determined in a separate portion, using the alkaline tartrate solution. The difference between the two determinations is the amount of potassium oleate consumed by the magnesium present. The potassium oleate solution must be standardized by means of a known magnesium solution, as the calcium and magnesium do not

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[a] See also the colorimetric method for magnesium.

react with it in chemically equivalent quantities, and the factor thus determined is used in calculating the amount of magnesium in the solution. This method is not very satisfactory when the magnesium is small in proportion to the calcium.

Carbonate and Bicarbonate.

The method employed for the determination of carbonate and bicarbonate has been discussed at length by Cameron [a] in connection with the estimation of larger amounts in the extracts from " alkali " soils. Normal carbonate is rarely present in waters and extracts of soils from the humid or semihumid regions; but bicarbonate is nearly always found, though generally in comparatively small quantities, thus necessitating the use of dilute standard solutions and observing certain precautions in determining the end point in the titration. One portion of the solution will serve for the determination of both carbonate and bicarbonate. The method depends upon the different action of phenolphthalein and methyl orange in the neutralization of these two substances. Potassium hydrogen sulphate solution is used for titrating, the first step being with phenolphthalein as indicator. The reaction is expressed by the equation:

$$Na_2CO_3 + KHSO_4 = KNaSO_4 + NaHCO_3.$$
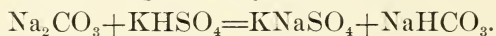
The point of neutrality is shown when all carbonate present is converted into bicarbonate. The second step is the titration of the bicarbonate formed in the first step together with that existing originally in the solution, using methyl orange as indicator. This reaction is expressed by the following equation:

$$NaHCO_3 + KHSO_4 = KNaSO_4 + H_2CO_3.$$
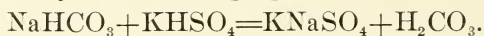
The point of neutrality is shown in this case when all bicarbonate has been decomposed.

Reagents required.

1. *Standard potassium hydrogen sulphate solution.*—Dissolve 5.58 grams of pure potassium hydrogen sulphate in water and dilute to 1 liter. Of this stronger solution dilute 100 c. c. to 1 liter. Each fiftieth of a cubic centimeter of this dilute solution, one scale division of the burette, is equivalent to 0.005 milligram of HCO_3 in bicarbonate, using methyl orange as indicator, and 0.00492 milligram of CO_3 in normal carbonate, using phenolphthalein as indicator.

2. *Phenolphthalein indicator.*—This is made by dissolving 1 gram of phenolphthalein in 100 c. c. of 50 per cent alcohol. As the phenolphthalein is slightly acid in character, the solution is made neutral by cautiously adding a few drops of centinormal alkali until very faintly red, and then adding a drop of centinormal acid.

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[a] Bul. 18, p. 77, Div. of Soils, U. S. Dept. Agr., 1901; Amer. Chem. Jour., **23**, 471 (1900).

3. *Methyl orange indicator.*—This is made by dissolving 1 gram of methyl orange (indicator) in 1 liter of water.

Analytical process.

(*a*) *Titration of carbonate.*—Into a short Nessler tube put 25 c. c. of the solution to be examined. Into a similar tube put 25 c. c. of distilled water. Add to each tube a drop of phenolphthalein indicator (2). If the solution to be examined is colored pink, carbonate is present and the solution is titrated with standard potassium hydrogen sulphate solution (1) to disappearance of the color. The reading is conveniently expressed in divisions of the burette, graduated into fiftieths of a cubic centimeter.

(*b*) *Titration of bicarbonate.*—A drop of methyl orange indicator (3) is now added to each of the above tubes, and the titration continued until the first indication of a reddish tinge is imparted to the solution. To determine this end point, the tube containing the solution titrated is carefully compared with the blank tube, by holding over a white surface, or viewing the tubes in the camera of the colorimeter. Some practice is necessary in order to get the end point sharply. The operator must be capable of very sharp differentiation of tint, and if with practice he can not succeed in duplicating readings with certainty to within two burette divisions (one twenty-fifth c. c.), it indicates that his eyes are not sensitive enough in differentiating these tints to safely use the method. To make sure that the end point has really been reached, the operator should take the reading, and then add two or three drops more of the acid solution. A well-marked red color should be produced, quite noticeable by comparison with the yellow of the blank.

(*c*) *Calculation of the carbonate and bicarbonate.*—The total titration for bicarbonate (*b*), less the titration for the carbonate (*a*), gives the titration for the bicarbonate originally present. The carbonate and bicarbonate are then readily calculated from the strength of the standard solution, and the volume of the test solution used.

Chloride.[a]

The chloride is determined by the usual titration with a standard silver nitrate solution, using potassium chromate as indicator. The small quantities usually met with in the investigations of soils of humid and semihumid areas necessitates the use of special precautions in determining the end point of the reaction when working with dilute standards.

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[a] See also the turbidity method for chloride.

Reagents required.

1. *Standard silver nitrate solution.*—Dissolve 2.3974 grams of pure silver nitrate in water and make up to 1 liter. Each fiftieth of a cubic centimeter of this solution, one scale division of the burette, is equivalent to 0.01 milligram of Cl.

2. *Potassium chromate solution.*—A saturated solution of carefully purified potassium chromate for use as indicator.

Analytical process.

Measure out 25 c. c. of the solution to be determined into a porcelain dish, preferably a good-sized casserole. Into a similar dish put 25 c. c. of water. The two dishes are especially selected so as to be identical in tint. To each dish then add two drops of the potassium chromate indicator (2) and titrate the unknown liquid drop by drop with the standard silver nitrate solution (1), stirring continually with a glass rod until a slight indication of a reddish tint is perceptible. This faint tint is not permanent when working with dilute solutions. By comparing with the blank, after a little practice, the end point is readily determined. It is advisable, however, to add two more drops of the silver nitrate solution after the end reading has been taken, so as to make sure that the end has really been reached. This amount in excess will produce quite a marked reddish tint in the solution in comparison with the yellow of the blank. The reading is conveniently expressed in the scale divisions of the burette.

If the amount of chloride is very small a larger volume of the solution can be taken and evaporated to approximately 25 c. c. and then titrated.

If the solution contains enough chloride to produce a marked turbidity when titrating it is advisable to use another portion of the solution to be tested as blank instead of the distilled water and adding the silver nitrate solution so as to reach nearly but not quite to the end point of the precipitation. This makes the comparison of the liquids easier and more certain. Instead of distilled water the liquid itself should be used as a blank when it is not entirely colorless.

The liquid used in this titration should be neutral. If acid, it must first be neutralized, nor should it ever be alkaline to phenolphthalein. The solution which has been used in titrating for carbonate and bicarbonate may be used in this test, but the color of the methyl orange interferes somewhat with the sensitiveness of the end point, and it is preferable, whenever possible, to use a new portion of the solution for the determination of chloride.

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